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EARTH MOVEMENTS ACCOMPANYING THE KATMAI ERUPTION. II

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SUMMARY

PART II. FRACTURING IN THE VALLEY OF TEN THOUSAND SMOKES

CHARACTERISTICS OF THE FRACTURES

Reference has been made several times in this paper to the formation of fractures in the Valley of Ten Thousand Smokes at the time of the eruption. Their formation was undoubtedly accompanied by earth movements of some importance. We shall now describe the more important features of the fractures, inquire into

their causes, and see if their formation can be correlated with the tectonic earthquakes that have been described.

Some of the features of the fissures, especially their relation to the hot sand-flow and to the fumaroles, have been described in previous articles.[1]

For the purposes of the present paper, a brief recapitulation of the pertinent data of previous articles will be given, supplemented with other information, much of which was gathered in the second visit to the region in 1923.

During the period of the eruption a broad, Y-shaped valley, bounded by abrupt mountains, and extending several miles northwestward with gentle slope from the foot of Mount Katmai and its neighbor, Mount Trident, opened in numerous fissures. These are believed to have been the source from which a great volume of hot pumice and fragmental glass (the sand-flow) was poured out, forming a phase of eruption similar in some respects to the *nuées ardentes*, or "glowing clouds," of the West Indian eruptions of 1902, and since then recognized as a not unusual volcanic manifestation. This valley in its transformed character is now known as the Valley of Ten Thousand Smokes.

The extruded material forms a tuff deposit covering the valley floor to a great depth—100 feet and possibly much more in places. The location of some of the fractures[2] is demonstrated with certainty by fault scarps, visible especially around the margin of the valley, and very prominent on Broken Mountain, near the head of the valley, immediately adjacent to the new volcano Novarupta (see Fig. 11). The presence of many other fractures and fissures has been inferred from the manner in which fumaroles are disposed in long, definite lines, the whole length of which may serve as a vent for

[1] E. T. Allen and E. G. Zies, *A Chemical Study of the Fumaroles of the Katmai Region*, "National Geographic Society, Contributed Technical Papers, Katmai Series," No. 2. Washington, 1923.

R. F. Griggs, *The Valley of Ten Thousand Smokes*. Washington, 1922.

C. N. Fenner, *The Origin and Mode of Emplacement of the Great Tuff Deposit of the Valley of Ten Thousand Smokes*, "Katmai Series," No. 1. Washington, 1923.

[2] Where fractures are spoken of, a break is meant, with no implication as to whether there was or was not a significant amount of movement of the sides; fissuring is intended to imply some spreading apart of the walls; while faulting implies significant movement of the walls past each other.

vapors, or the exhalations may be concentrated at certain openings. This linear arrangement shows as a prominent feature in photographs taken by Griggs in his earlier explorations, and was still plainly evident in 1919. With the diminution of activity in 1923 it was not so perceptible, but was still visible in places (Fig. 5.). Frequently the orifices of continuous lines of fumaroles[1] are merely cracks in the tuff deposit a few inches in width, but they extend downward indefinitely, as is shown where deep stream gullies inter-

FIG. 5.—Looking northerly down the Valley of Ten Thousand Smokes from the base of Mount Cerberus. Linear distribution of fumaroles is evident. The photograph was taken on a damp day when visible condensation of steam from the fumaroles was a maximum. (Photo. by C. N. F., 1923.)

sect ther Occasionally, the orifices are open to a width of several feet, and one may look down to obscure depths. Fumarolic action was very vigorous when the valley was discovered by Griggs in 1916, and was still strong during the investigations of 1919. By 1923 activity had diminished very perceptibly.[2] Though the life of the fumaroles appears likely to be short in the valley as compared with

[1] For convenience, the description of the arrangement of fumaroles, on which inferences regarding fracturing are based, is given as if the activity visible in 1919 were still continuing in full force.

[2] Cf. Fig. 5 with the illustration on p. 234 of Griggs's book, *The Valley of Ten Thousand Smokes*. In the latter illustration observe also the alinement of fumaroles.

some other regions, the evolution of magmatic gases in quantity over a period of several years, and the many high temperatures found by Allen and Zies in 1919, point to a source for the emanations other than the superficial tuff deposit, and indicate a derivation from an underlying body of magma. The pumiceous character of the superficial tuff suggests that its supply of volatiles was practically exhausted during eruption. Emanations from it may have continued for a brief period after its emplacement, and may have

FIG. 6.—Portion of an east-west fault (along zone shown in Fig. 12) in the terraces at the southern head of Mageik Basin. In the photograph the lower deposits are indurated sand-flow tuff; above are irregularly stratified beds containing great blocks of sand-flow material thrown out by explosions. The camera faces the fault scarp. (Photo. by C. N. F., 1923.)

given rise to certain short-lived fumaroles of which evidences were visible in 1919, but which had already become inactive. It is very doubtful if any of those still vigorous at that time were of this derivation.

A feature of significance in its implication that the fracturing resulted in open fissures, which formed eruptive vents and supplied the material of the sand-flow, is shown in many places by explosive effects seen in direct association with them, as is illustrated in Figures 6, 7, and 8. In Figure 6 angular blocks of consolidated sand-flow material, many of them of great size and weighing many tons, have

been thrown out of a fissure and now lie on the surface along the borders. A slightly different phase of explosive action along fissures is shown in other places by lines of large craters blown out of the tuff deposit and surrounded by mounds of *ejecta*. A crater of this kind appears in Figure 7. In places the craters are so close together that their arcs intersect. They frequently occur in situations where explosions due to the contact of hot tuff with water or marshy ground appears

FIG. 7.—A large explosion crater in the sand-flow tuff in the southeastern arm of the valley. The sand-flow is overlain by the stratified ash-fall from Katmai and Novarupta, but above this are strata of materials blown out of the adjacent crater, and containing blocks of sand-flow. In 1919 some of the craters in this area were still evolving clouds of steam, but in 1923 all were practically dead. (Photo. by C. N. F., 1923.)

very unlikely.[1] Figure 8 shows a portion of a line of craters close to the base of the falling cliff of Falling Mountain. The indication of explosive action here at just the place where a major fissure is inferred from the occurrence of the Falling Mountain landslide seems very significant. In explanation of these associations of explosive effects with fissuring it is inferred that after the violent extrusions of pyroclastic tuff that formed the sand-flow abated, feeble explosions continued at some of the orifices, and resulted in clearing out

[1] Explosive effects, probably due to the latter cause, are found in places, but may generally be differentiated.

again for a short time the material that choked the openings.[1] Subsequently, less violent evolution of gases and vapors continued for years in the form of fumaroles.

Near the head of the valley, in the area around Novarupta, fracturing was not confined to the valley floor, but affected the adjacent high country also. The prominent faults on Broken Moun-

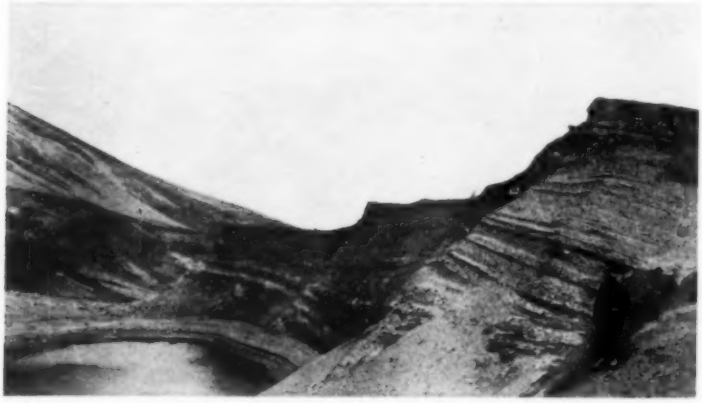

FIG. 8.—Explosion craters at foot of the northern cliff of Falling Mountain. The section of strata at the right shows regularly stratified ash-fall from Novarupta and Katmai, overlain by irregularly stratified beds of *ejecta* from the immediately adjacent craters. The broken cliff of Falling Mountain is to the left of the view. (Photo. by C. N. F., 1923.)

tain have been mentioned, and the adjacent lower slopes of Mount Trident also were faulted; and both of these localities became the scene of strong fumarolic activity. Undoubtedly, similar movements were responsible for the landslide from Falling Mountain. The

[1] A problem which is of interest, but will not be discussed in detail here, relates to the agencies that caused the fragmental material of the sand-flow to become cemented into the firm mass that we see in many places. This is its usual condition in the upper valley, and in places in the lowermost part of the deposit in the lower valley. This cementation apparently took place almost immediately after extrusion, for the *ejecta* of the waning phase of explosions contain angular blocks of indurated material. Possibly the induration was due to cohesion of the fragments of hot glass, such as is known to take place in commercial glasses at temperatures well below fluidity, or possibly chemical action of vapors may have been a factor. Among the masses of rhyolitic glass in Novarupta dome tightly welded crush breccias are found.

débris from this was covered by the sand-flow and is not visible, but a great scar has been left on the northern face of the mountain, from which small masses of rock continue to break away and plunge down, and cracks from which vapors issue are still active. An offshoot of the main area of fissuring is inferred to have followed the low divide of Katmai Pass also.

These last-mentioned occurrences comprise the only important areas outside of the valley floor in which recognizable fracturing has taken place, but several others of relative insignificance should be mentioned for completeness. On the westward-facing cliffs of Baked Mountain little seeps of steam were visible in 1919, and were still continuing in 1923. They issue high up on the cliffs, and examination shows that the orifices are merely joint cracks. There are indications that a similar leakage of vapors may at one time have been rather general on Baked Mountain. On the opposite side of the valley, on the lower slopes of Buttress Mountain (above the margin of the sand-flow), several small fumaroles were active in 1919, and were noted by some of the members of the expedition. I did not visit their site at that time, and in 1923 they had apparently ceased.

A certain amount of interest attaches to some of these minor vents, in that the vapors visibly rise from the bed rock. In the main areas of the valley there is no reasonable doubt that the fumaroles have a similar origin, but the superficial covering of tuff conceals it from actual vision.

With the exceptions noted, the fracturing is confined wholly to the valley. If a map were drawn on which were represented the fractures inferred from the alinement of fumaroles and from visible faults, a large area showing a network of cracks would be blocked out, which would practically coincide with the main part of the valley; and if the rather minor exceptions mentioned were disregarded, no fracture would be found outside of its boundaries. In the early years of exploration of the area fumaroles were numerous almost to the margin of the "high sand mark," and there stopped abruptly.

A feature believed to be of much significance is the fidelity with which fractures and faults follow the margins of the valley for long distances, even outlining projections and embayments, but do not

pass into the adjacent hills. An instructive example is afforded by fissures along Baked Mountain. The western side of this eminence is marked by prominent fissures lying close to the mountain, some of which are open cracks and others are indicated by lines of fumaroles. At the southern end of the mountain, where the cliffs swing abruptly through more than a right angle to form the northerly side of Novarupta Basin, this set of fractures continues only a short distance out into the valley, and another set of prominent intersecting fractures, along which there is still fumarolic activity, starts at this point and follows the base of the cliffs eastward into the basin. In a similar manner the curving shore of Mageik Basin[1] is paralleled by fractures. These may be considered to begin with northeast and southwest fissures at the base of the northwestern face of Mount Cerberus. As the contours of Cerberus swing southward, the first fissures are succeeded by north and south fissures lying nearly parallel to the western face of the mountain and extending nearly to the base of Mount Mageik at the southern head of Mageik Basin. Along the foot of Mount Mageik, east and west faults with vertical throws of 30 or 40 feet are prominent, but they come to an end in the southwest angle of the basin, and another set, intersecting them at nearly a right angle, extends northward at the foot of the eastward-facing cliffs of Buttress Mountain. These last are marked by faulting at their southern end; northerly they are shown only by exudations of steam, but indications of them persist continuously for about 5 miles.

The general restriction of fractures to the floor of the valley, and the intimate relationship that fracturing bears to this topographic depression, seem to indicate that the forces which caused the fracturing were local, and were situated at a comparatively shallow depth.[2] In previous papers I have ventured the hypothesis that the effects were due to the intrusion of a sill of magma, pre-

[1] Mageik Basin is the area at the head of the southern arm of the valley, just below Mount Mageik.

[2] It is interesting to contrast the relations here with those of certain regions in Iceland, so well described by Thoroddsen (*Island: Grundriss der Geographie und Geologie*, Gotha, 1905), where the fractures are undoubtedly fundamental. For instance: "The fissures always run in a straight direction without regard to the relations of the terrain, and in spite of small bends and curves always maintain the principal direction" (p. 118).

sumably derived from the same body that caused the eruption in Katmai crater, driven between the horizontal sedimentary strata underlying the valley. Where the roof above the intrusion was comparatively thin it was uplifted and fractured, but where the heavily loaded mountain areas at the sides of the valley were encountered an obstacle was met which opposed an effective resistance to further advance of the intrusion. For this reason, the fracturing was in most places restricted to the floor of the valley. The upheaval and fracturing of the roof allowed the escape of a portion of the magma, probably in a succession of outbursts lasting for a few hours. This was the hot sand-flow.

It is naturally inferred that the intruded body was derived from a source lying beneath the sharply defined volcanic zone along which Katmai, Trident, Mageik, and other volcanoes are situated. The form of the channel through which the magma rose from the subcrustal reservoir to the upper lithosphere can only be surmised. It need not necessarily have been the same conduit that supplied the material for the immediately succeeding eruption at Katmai crater; in fact, the thorough manner in which a limited area of the lower slopes of Trident was fractured gives a hint that it was at this point that the magma, which had probably risen through some steeply inclined fissure, found an escape to the side, beneath the strata of the valley. It may be for this reason that the immediately adjacent portion of the valley was so greatly disturbed. Here not only was the floor shattered, but considerable portions of Broken Mountain and Falling Mountain were greatly fractured, and the vent of Novarupta was established. The great amount of disturbance of this area seems to point to a greater impelling power acting upon the magma here than was later shown when intrusion had carried it under the wider spaces of the valley proper. In this later movement resistance to spreading beneath the floor seems to have been comparatively small and the adjacent mountains were hardly affected. They were disturbed only to the extent of opening up joint cracks to a slight amount in a few places.

This picture of the process need not necessarily be accepted in all its details. The essential feature to which attention should be directed is the disturbed condition of the valley floor in contrast with

the relatively undisturbed condition of the surrounding mountains, and in explanation of this the hypothesis of the intrusion of a sill-like body has been formulated.

Novarupta seems to have been a vent essentially similar to the many other orifices of extrusion of sand-flow tuff, but in this case the opening became so enlarged that great quantities of pumice and ash were ejected, followed by the welling up of a mass of viscous lava to form the dome. In its neighborhood fissures are very prom-

FIG. 9.—Fault graben in the area east of Broken Mountain. Mount Trident in background. (Photo. by C. N. F., 1923.)

inent, and fumarolic action has continued to the present time in more activity than elsewhere.

The movements along the faults in the valley appear ordinarily to have been simple vertical throws, but may take other forms. In the area to the northeast of Novarupta sunken blocks or gräben occur. One of these is shown in Figure 9. It forms a trough, probably 10–15 feet deep, running diagonally down a smooth slope of moderate inclination. Other faults in this vicinity are steplike. They run in various directions. The upper part of Broken Mountain, just to the north of Novarupta, is broken by numerous large faults. A sketch of one of these is given in Figure 10. It has the form of a sunken wedge with stepped faults at the sides. A photographic view

of the northeast wall of the same fault appears in Figure 17. The general appearance of a portion of Broken Mountain, showing some of the prominent faults, may be gained from Figure 11.

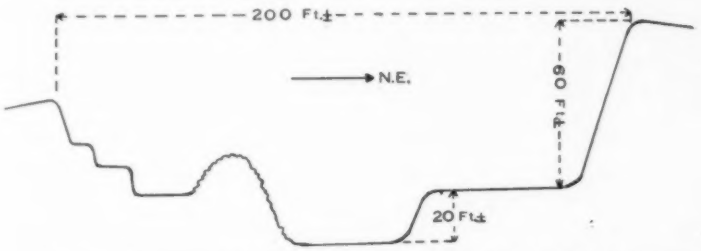

FIG. 10.—Diagrammatic sketch of faulting on Broken Mountain. The height and width of the benches vary along the fault.

FIG. 11.—Looking downward from Baked Mountain upon Novarupta and the southern portion of Broken Mountain. Several of the large faults of Broken Mountain, which have throws of as much as 60 or 80 feet, are visible. (Photo. by C. N. F., 1923.)

With the exception of a few places previously noted, all of the areas of fumarolic activity and fracturing that we have been considering are heavily overlain with tuff, and the visible portions of the fractures are in these deposits of fragmental *ejecta*. In the ele-

vated areas near Novarupta the sand-flow deposit is absent, but there is a thick mantle of pumice and ash from that vent and from Katmai. The throw of the faults is not sufficient to bring up the underlying rock. In the main part of the valley a great thickness of sand-flow deposit covers the floor, and the fault scarps do not reveal what is beneath. It is beyond reasonable doubt, however, that faults of such large throw are more than superficial phenomena, and must penetrate the rock-strata below.

One important consequence arises from the presence of these thick layers of tuff, and should be noted: The visible record reveals only the movements that took place after the eruption was nearly or quite at an end. If, as we believe, the first important episode of the eruption was the upheaval of the valley area, this was followed almost immediately by the outpouring of the sand-flow, and shortly afterward by the heavy downfall of *ejecta* from Katmai and Novarupta. Whatever displacements may have accompanied the initial fracturing of the rock strata, they were almost at once concealed by the smooth mantle of *ejecta*. We know from the description given by Spurr that when he traversed the valley in 1898 it showed a somewhat varied topography, with "great walls of moraine, damming mountain gorges," but all this disappeared beneath the pyroclastic deposits. The great avalanche from Falling Mountain also was buried and completely concealed.

UPLIFT AND COLLAPSE OF THE VALLEY FLOOR

Because of these facts there is no direct evidence of the character of the initial displacements accompanying the formation of the fractures. One would infer that if a sill was intruded beneath the floor, the first movement was an upheaval, which was followed by partial subsidence as a portion of the intruded magma found escape through the fissures, and that only the subsidence is recorded in the fault scarps.

The remarkable feature to which the term "high sand-mark" has been applied may probably be explained as a result of the final faulting and settling. The high sand-mark is the top of a terrace or slope which follows the margin of the sand-flow in much of the

valley area.[1] In the southern arm of the valley it is especially well developed, but occurs in many other parts of the valley also, and in places is practically continuous for many miles. This marginal bench is composed of the same material as the general body of sand-flow, but reaches 200 feet (locally even higher) above the flat areas of the adjacent floor, to which it descends by a slope of 10°–15°. This elevated margin shows that the sand-flow, at the time of extrusion, attained a level considerably above its present general surface, and an explanation is required as to the manner by which its surface became depressed.

Griggs, in his early papers, regarding the sand-flow as an extrusion of mud, supposed the "high mud-mark" to indicate the height which the fluid reached at first, and at which a marginal portion was left after the level of the major portion had been reduced by draining away.[2]

Later, when the sand-flow had been more thoroughly studied and its origin as an outburst of incandescent material had been recognized, I suggested that the high sand-mark indicated the level of the deposit while in loose form, and that the process of settling together of the loose particles had reduced the general level.[3]

Further investigation in 1923 made this explanation seem inadequate and brought anomalies to light. Especially noteworthy was the evidence that the sand-flow tuff had become well indurated prior to the fracturing that accompanied the downward movements. It had assumed such firmness that neither flowage nor shrinkage would be likely to affect it. Moreover, certain phenomena were found which pointed strongly to another explanation.

Around the margin of Mageik Basin the high sand-mark is everywhere a prominent feature, and the marginal faulting of the basin that has been described occurs near the edges or part way down

[1] The characteristic appearance of the high sand-mark may be seen in the photograph on p. 262 of *The Valley of Ten Thousand Smokes*.

[2] R. F. Griggs, "The Great Hot Mud Flow of the Valley of Ten Thousand Smokes," *Ohio Jour. Sci.*, Vol. XIX (1918), p. 121.

[3] C. N. Fenner, *The Origin and Mode of Emplacement of the Great Tuff Deposit of the Valley of Ten Thousand Smokes* (published by the National Geographic Society), p. 12.

the slopes of the terraces.[1] On the western side of the basin, at the foot of Buttress Mountain and very near the edge of the high sand-mark, a fault, having a throw of 30–35 feet and easily seen from a distance of 2 or 3 miles, lies parallel to the cliffs for about 1½ miles. Toward its northern end the throw diminishes, and the fault apparently passes into fractures or fissures, which continue along the terrace for several miles farther and are marked by exudations of steam. Along the part of the course where the walls of the fault are visibly spread apart, the structure is well shown, and the relations appear as in Figure 13. The strata of the sand-flow lie nearly horizontal for the short distance from the cliffs of the mountain (on the right) to the fault; there is then a gaping opening, and a drop of the block on the valley side, together with a down-tilting toward the valley. The relations suggest that the whole floor of the valley has collapsed, leaving a marginal rim to indicate the height at which the surface stood.[2]

The high sand-mark, accompanied by marginal fracturing, has been traced around the sand-flow in the whole southern arm of the valley, almost without interruption. In many places evidence of vertical movements in these fractures is apparent, and the downthrow of the faults on the eastern, southern, and western sides is always toward the middle of the valley (cf. Figs. 12, 13, 14, and 15). Elsewhere vertical throws are not evident, but lines of fracturing, frequently accompanied by fumarolic activity, appear in the marginal terraces, or traverse the slopes that connect the high sand-mark with the floor of the valley (see Fig. 16). Such is the case along the western side of Baked Mountain. Here no vertical throw is perceptible, but there are open fumarolic fissures, several feet wide, whose walls can be seen to spread apart slightly as they approach the surface. There is reason to suspect that these marginal fissures may exist in many places where their presence would be inferred but cannot be seen. The winds prevalent in the valley constantly shift the

[1] Griggs noted that "All around the margin of the Valley, just below the 'high water mark,' runs a series of gaping fissures, as though the surface had been stretched by subsidence after its formation." See "The Great Hot Mud Flow of the Valley of Ten Thousand Smokes," p. 123.

[2] Other views of the same fault zone are shown in *The Valley of Ten Thousand Smokes*, opposite p. 225 and on p. 232.

surface sands, and tend to fill orifices in which the upward rush of steam is not strong. It is not unusual to find a well-developed fissure

FIG. 12.—Line of faulting, A–B, in the marginal terraces of the sand-flow, at the northern base of Mount Mageik. (Photo. by C. N. F., 1923.)

FIG. 13.—Looking southerly along the fault that follows the elevated margin of the sand-flow on the western side of Mageik Basin. Shows effect of collapse of the valley floor, with down-tilting of blocks on the left side of the fault, toward the middle of the basin. The vertical faces of sand-flow deposit in the foreground are about 30 feet high. Mount Mageik in the background. (Photo. by C. N. F., 1923.)

FIG. 14.—View easterly from the middle of Mageik Basin toward Mount Cerberus (about 1¾ miles distant), showing elevated margin of the Basin ("high sand-mark"). This elevated rim here has the form of two broad terraces, broken by longitudinal faults (see Fig. 15), and rises to more than 200 feet above the flat floor. (Photo. by C. N. F., 1923.)

FIG. 15.—Looking northerly along a fault in the elevated margin of the sand-flow, on the eastern side of Mageik Basin. (Photo. by C. N. F., 1923.)

with fumarolic openings only occasionally appearing, the spaces between being filled with pumice, and the surface leveled off. In the light of these inferred phenomena of collapse and marginal fracturing, we seem to see the significance of the fact mentioned on an earlier page that great fumarolic activity reaches nearly to the edge of the high sand-mark, and there abruptly ceases.

If the inferences drawn with regard to the significance of the high sand-mark and its structures be correct, a drop of the valley floor to the amount of about 200 feet after the first uplift is indicated.

FIG. 16.—Small gullies, transverse to slope, and indicative of fissuring, in the northeastern marginal portion of Novarupta Basin. In the background, a part of Falling Mountain at the left, and Mount Cerberus in the center. (Photo. by C. N. F., 1923.)

This evidently occurred after the extrusion of the bulk of the sand-flow, though minor outbursts may have continued and served to smooth out small irregularities in the surface of the depressed floor.

The structure of the marginal terraces has been studied especially in the southern arm of the valley, but there is no reason to doubt that the same structure characterizes the terrace wherever it occurs. The terrace is found not only in the southern arm of the upper valley, but also in the main valley for several miles below the junction of the arms. In the lower valley the high sand-mark is a less prominent feature. In Knife Creek Valley (the southeastern arm

of the upper valley) the high sand-mark is well developed at the lower end, but becomes obscure or disappears toward the upper end. Its constant association with the sand-flow over so much of the occupied area indicates its importance as an essential feature.

AN UNDERLYING BATHOLITH UNLIKELY

A collapse of the roof appears a likely consequence of the escape of magma from an underlying sill. Possibly it, by itself, is not out of accord with the idea that a larger body, such as a batholith, which had risen close to the surface, was the source of the extrusions. Such a hypothesis demands, however, that after the episode of eruption there was no further tendency for the material of the batholith to rise or be forced to the surface. It would seem that external pressures, or the internal tendency to expand from the presence of volatiles, would lead to a different result in the case of a practically inexhaustible batholith.

Griggs[1] has favored the idea that a batholith of regional extent and tens of thousands of feet thick had been intruded beneath the area. In order to account for the evident differences in amount of disturbance between the valley and the mountains, he supposes that the intrusion had approached the surface closely over a large area,[2] so that surface features exercised control over fracturing. One or two geologists in conversation have suggested a similar idea. For reasons more direct and less hypothetical than those mentioned above, I doubt if this explanation is tenable.

In discussing the question we shall have to discriminate between two forms which might be assigned to the batholith. In one, the upper surface may be supposed to have a widely extending horizontal form; in the other, there is an upward protrusion or stock which underlies an area not much greater than the valley, while beyond this the sides drop steeply.

If a widely extending batholith rose (by stoping or otherwise) so close to the surface as to cause the general fracturing of the roof that we see, the blocks thus separated from each other would be left with no effective support other than the body of magma below, and,

[1] *The Valley of Ten Thousand Smokes*, chapter beginning on p. 287.

[2] *Ibid.*, p. 301. See also his sketch of inferred conditions, shown on p. 263.

from ordinary laws of flotation, should sink into it until they displaced equivalent weights of liquid. Now the valley area is nearly surrounded by mountains, rising from 1,500 to 5,000 feet above the immediately adjacent floor, within distances varying from 1 mile to 3 or 4 miles. Moreover, if we pass outside of the area closely adjacent to the valley, and survey the surrounding country that would be underlain by such a batholithic body, we find a topography of great relief, in which high and rugged mountain blocks alternate with broad valleys similar to the Valley of Ten Thousand Smokes.

As long as the roof of the batholith was intact and no escape of the liquid body was possible, it would be able to support the superincumbent load, but as soon as fracturing occurred in the valley, this ability would disappear, and the condition would be that of mountain blocks rising from a shelf which projected horizontally over the batholith, presumably for several miles (depending upon the dimensions assigned to the body), and unsupported except for connection with the rock masses beyond the edges of the batholith. It seems only necessary to state these conditions to realize what a mechanically impossible situation is presented. Under such circumstances, rupture along joint planes, involving the whole region, should result. The mountain blocks should settle at least hundreds or more likely thousands of feet, and a corresponding amount of liquid would be forced up in the intervening low areas.

If the conception be modified so that only a stocklike protuberance of the batholith be supposed to extend upward to near the surface, undermining an area not much greater than that known to be fractured, the scale of necessary readjustment would be lessened, but would still be of great magnitude. Baked Mountain, Broken Mountain, Falling Mountain, and Mount Cerberus, lying practically within the valley area, rise approximately 1,500 feet above their immediate surroundings. Baked Mountain and Broken Mountain especially are completely surrounded by areas of fracturing, and Mount Cerberus is nearly surrounded. They should have settled deeply in the batholith. Buttress Mountain, also, a high, narrow ridge bounded by the main valley on the east and by the valley of Windy Creek on the west; and Falling Mountain, cut off from Mount Trident to the rear by a depression not much higher

than the valley floor, might be expected to break off and settle in a similar manner. Instead of such great downward displacement of mountain masses, we find that in the latest movements (the only ones of visible record) the floor of the valley settled slightly, as might be expected with the outflow of a portion of a sill. In the section around the head of Novarupta Basin the movements involved slices of the adjacent eminences, but this does not affect the conclusions. With a batholith the whole of these mountain masses should have dropped to such a degree as to show an evident topographic unconformity with relation to their surroundings.

The sill explanation is not demonstrable, as the manner in which the various phenomena of igneous intrusion exposed by erosion around ancient volcanoes express themselves in surface effects is little known. It has seemed desirable, however, to make an attempt at interpretation of the surface effects, and the sill hypothesis has been favorably considered because the observed phenomena seem to accord with it. Indirectly, it has been strengthened by the difficulties that other hypotheses have to meet. Since it was first suggested in 1920 the probabilities in its favor appear to have been considerably strengthened with developments and with the acquisition of additional information. The waning of fumarolic activity in the period from 1919 to 1923 indicates that the mass of hot material is not of great dimensions. It is hardly possible to make a useful calculation of the rate at which heat would be transferred from a mass of hot rock, fractured to an unknown degree, to its surroundings and to penetrating meteoric water; but we know that in certain regions, such as Yellowstone Park, Iceland, New Zealand, the Mount Lassen region, or Tuscany, geysers or fumaroles have been active on a large scale for hundreds or thousands of years, and in such instances it is natural to infer that the bodies of hot rock from which they derive their energy are large. But in the Valley of Ten Thousand Smokes the diminution of activity from 1912 to 1923 is estimated (from the number of dead fumaroles and from the diminution of activity actually seen) to have been as much, at least, as two-thirds of its original magnitude, and this does not seem consistent with the presence of a great mass of hot rock.

LACK OF COMPARATIVE DATA ON ELEVATION OF THE VALLEY BEFORE AND AFTER THE ERUPTION

Considered in relation to the fracturing and faulting in the valley, the hypothesis of a sill probably implies that the floor was first uplifted and broken into blocks, that a portion of the magma escaped through the fissures in a succession of outbursts and formed the sand-flow, thus concealing the evidences of upheaval, and that as a consequence of the escape of material from below the floor subsided, but not to its original level.

In connection with these inferred movements of the floor some comment seems to be called for on arguments presented by Griggs in his *Valley of Ten Thousand Smokes*.[1] In arguing against the presence of a sill he says that the surface would be upheaved, and probably much broken, when the sill was squeezed in, and states, as a chief argument against a sill:

> No appreciable changes of altitude occurred at the time of the eruption. The precise triangulation of the Coast and Geodetic Survey gives us information as to the elevation of the high peaks in 1908. These altitudes have been checked against many observations by our surveyors and found to be unchanged within the limits of a few feet.

The inference that would be drawn from this statement is that data exist by which a comparison can be made between levels before and after the eruption, and that this comparison is sufficient to show that no significant change of level has occurred in the area that would be underlain by a sill. Unless this inference is intended the argument does not seem to be relevant.

I have taken pains to learn what data on elevations had been obtained by the Coast and Geodetic Survey prior to the eruption.[2] It was found that all the essential data of the Survey that have a bearing on the matter are shown on Chart 8555. This gives the position and elevation of several peaks visible from Shelikof Strait, as obtained by triangulation, namely, three peaks of Mount Mageik, two peaks of Trident, three peaks of Katmai, and Knife Peak. In

[1] Principally on p. 303.

[2] In this matter Colonel E. Lester Jones, director of the Survey, Major William Bowie, chief of the Division of Geodesy, and other members of the staff, gave me great assistance. The records were looked up, and sources of information ascertained.

addition, the general configuration of the neighboring topography is indicated approximately by dotted form lines, with no figures of elevation attached. These were intended merely to suggest the topography. In part, they were probably sketched from the deck of a vessel in Shelikof Strait; and, in part, are based on the sketch map made by Spurr's party in their journey through the valley in 1898.[1] No accurate mapping is attempted on the chart, except for the triangulated peaks mentioned, and no surveys had been made which would serve as a basis for this.

The several expeditions sent out by the National Geographic Society did a large amount of topographic work, and the results were published on a map accompanying Griggs's book. It is noted on this map that the triangulation and photography are based on United States Coast and Geodetic Survey stations. This implies that the position and elevation of previously determined peaks were accepted as correct, and the surveys continued on this basis. Accordingly, we find that the peaks of Mageik and Trident are shown with the same figures of elevation as on the chart of the Coast and Geodetic Survey. The peaks of Katmai disappeared in the eruption, and no comparison is possible. The elevation of Knife Peak is not given in figures, but contour lines represent it as 215 feet or more higher than on the chart. The discrepancy in the last case may be due to the fact that the determination by the Coast and Geodetic Survey was made by only one intersection, and the record with respect to it is annotated "no check." Necessarily an error in the altitude of Knife Peak was made either by the Coast and Geodetic Survey or by the topographers of the National Geographic Society, or else the elevation has changed. These data apparently cover everything on which Griggs's statement is based. Their consideration shows that the information does not support arguments in opposition to the injection of a sill. There are no comparative data relating to the valley floor or to those areas closely adjacent to it that might be supposed to have been uplifted by the intrusion of a sill.[2]

[1] J. E. Spurr, "A Reconnaissance in Southwestern Alaska in 1898," *Twentieth Ann. Rept. U.S. Geol. Surv.*, Pt. VII, map inset between pp. 140 and 141.

[2] Other arguments used by Griggs in support of his batholithic hypothesis are not sufficiently related to the present subject to be discussed here, but will be taken up in a subsequent article.

TECTONIC EARTHQUAKES NOT DUE TO FRACTURING IN THE VALLEY

Whether or not the hypothesis of a sill offers the correct explanation of outbursts in the valley, it is evident that much fracturing and faulting of the rock floor occurred. In endeavoring to determine whether this was the cause of the earthquakes that affected distant seismological stations, it is important to consider the time at which the fissures opened, with respect to the sequence of events. From Table I (Part I) it is seen that for at least a month prior to the eruption there is no record at distant points of shocks originating in the region. The first shock of this kind, directly related to the eruption, of which there is indication, is that of June 6, at 12 hours, 41 minutes. The information regarding this is a press report that a shock was felt then at Seattle Observatory. Klotz's compilation does not refer to a shock at this time at the observatories listed by him. If the report is well founded, the shock was nearly coincident with the first great outburst of the volcano as seen from the Steamer "Dora." If the opening of fissures in the valley and the outburst of the sand-flow preceded the eruption of Mount Katmai, the accompanying shocks were not of a character to give a satisfactory record at far-distant stations. None are recorded in Klotz's compilation, and the records of the Harvard station are a blank between June 3, 3 hours. (unknown source), and June 6, 18 hours.[1]

The most convincing evidence that the fissures opened prior to the eruption of Katmai is that the layers of ash from Katmai that cover the adjacent region cover the sand-flow in the valley also. There is no difference of opinion on this matter among those who have studied the relations. This can only mean that the sand-flow preceded the main eruption, and that the fracturing associated with the extrusion of the sand-flow did not give rise to the well-defined seismic disturbances at distant observatories which later movements registered.

[1] Griggs mentions (*Valley of Ten Thousand Smokes*, p. 23) information received from the seismographic station at Victoria, B.C., to the effect that the Milne seismograph there recorded a large number of quakes on June 6 and 7, most of which appeared to have their origin in the Katmai district. This station is only 1,450 miles from Mount Katmai, and shocks might have been distinguishable there which were not recorded at more distant points. It would be interesting to know when these quakes began, but I have not yet been able to obtain information on this point.

Martin recorded that on June 5, late at night, observers at Cold Bay noted that the northern sky looked black and stormy, though the weather on the coast was fair. This may probably be referred to the outbreak in the Valley of Ten Thousand Smokes. The first outbreak of any importance from Mount Katmai seems to have been at 1:00 P.M. on the sixth.

During the summer of 1923 I obtained an interesting account from Mr. Bob Scott, a prospector who happened to have been at the native village of Savonoski, at the head of Naknek Lake, when the activity began. According to him, no one there had noticed earthquakes or heard noises or recognized any premonitory symptoms before the eruption began. The day before had been clear, and the people that night had gone to bed expecting nothing unusual. Early in the morning (hour unknown, but light had appeared) the outbreak came suddenly, with great noises and earthquakes, which were almost continuous. He said there seemed to be something different about these quakes from those in which an earthquake wave passes over an area, but could not define the difference. Almost at once the air became filled with dust, so that it became perfectly dark. No light from the eruption was visible, and in any case could not have been seen because of the dust. The natives were in panic, and started down the lake in boats immediately, leaving many of their possessions behind. They kept close to the shore so as not to become lost.

This brief account does not add much detail to our knowledge of the eruption, but it supports the view that the fissures of the valley opened in the early morning of June 6.

The lack of seismographic record at distant stations of the fracturing of the valley floor is probably what should have been expected. C. G. Knott, in his treatise on earthquakes, says:

> The destructive character of an earthquake as experienced at the epicenter depends directly on its intrinsic intensity and inversely on its depth. A deep-seated but powerful disturbance might have less destructive effect at the epicenter than a shallow but much less powerful disturbance. The former would be recorded on delicate seismographs all over the earth's surface, while the latter might affect delicate instruments only within a comparatively limited area.[1]

[1] C. G. Knott, *The Physics of Earthquake Phenomena* (Oxford, 1908), p. 98.

The lack of record confirms the view that it was essentially a superficial phenomenon.

If Mr. Scott's recollections are accurate, the fracturing came suddenly, and was not preceded by recognizable earth movements at Savonoski, only 10–15 miles from the valley and 21 miles from Mount Katmai. It appears from this that the earthquakes felt at Uyak, Kanatak, and Nushagak, 56–131 miles distant from Mount Katmai in various directions, on June 4–5, were not directly related to movements either in the valley or at the volcano. Minor tectonic disturbances seem a likely explanation. The connection of the explosions noted at Seldovia and Nushagak on the morning of June 6, with outbursts in the valley, seems more probable. Regarding the earthquakes occurring on the same day, some doubt is felt, but, on the whole, it does not seem that they are to be referred to outbreaks in the valley or at the volcano. This is the inference drawn from evidence presented on previous pages, relating to the occurrence of loosely hanging rocks in cliffs in this neighborhood, which seems to show that neither the outbursts at Mount Katmai nor the upheaval of the valley floor were of the character to give rise to distinct earthquakes at distant points. Undoubtedly, the explosions accompanying the eruption of Katmai were of very great violence, and the uplift of the valley floor produced violent shocks in the areas actually fractured, as is shown by the total disruption of the slice of Falling Mountain that was involved; but the violence was not exerted in such a manner or at such depth as to affect severely even the immediately contiguous territory. No displacements of such great masses of rock as are involved in tectonic earthquakes were caused by them. The tectonic earthquakes that actually occurred during the eruption, and to which the shocks felt at distant points are seemingly to be referred, should be ascribed to the operation of other processes.

COLLAPSE OF THE FLOOR APPARENTLY GRADUAL

A feature of the faulting not yet referred to is of significance. The great faults on Broken Mountain have throws of as much as 60 or 80 feet in some cases. An idea of their magnitude may be obtained by reference to Figures 11, 17, and 18. The southern por-

tion of the mountain (the side toward Novarupta) has been broken to pieces by faults running in various directions, only a few of which are shown in the photographs. At the surface the fault scarps intersect beds of gravelly pumice of only slight coherence, but, in spite of this, relatively little of the material of the walls has been dislodged to form talus slopes. (See Figs. 17 and 18; also the photograph on p. 244 of Griggs's *Valley of Ten Thousand Smokes* and that on p. 46 of Fenner's *Origin and Mode of Emplacement of the Great Tuff Deposit of the Valley of Ten Thousand Smokes*.) From our knowledge of the

FIG. 17.—Wall of a fault of large throw in strata of pumiceous *ejecta* on top of Broken Mountain. Height of wall is about 60 feet. (Photo. by C. N. F., 1923.)

great dislodgments that violent earthquake shocks cause, as contrasted with the comparatively little disaggregation of strata seen here, we are led to ascribe only moderate intensity to the shocks accompanying these movements. It has been pointed out that these scarps do not record the initial fracturing but only the movements after the pumice beds were deposited. The initial fracturing may have been rather violent, but the final readjustment seems to have been gradual.

On nearly all sides of Novarupta there are indications of a settling of the surface toward that vent. On the northern or Broken Mountain side, the total throw of the faults is probably 200 feet

or more. On the east, there is a zone of complex faulting running for a considerable distance from the southeastern side of Broken Mountain in the direction of the western peak of Mount Trident, and the total movement here also has been large, though probably considerably less than on Broken Mountain. To the south of Novarupta, faults are visible on the lower slopes of Mount Trident, swinging around toward Falling Mountain. The throw of these appears to be less again than in the zone just mentioned. On the western side of Novarupta, there are steaming fissures, but it is only very close to

FIG. 18.—Pumiceous strata, chiefly from Novarupta, along a fault scarp on Broken Mountain. Height of wall is about 40 feet. Steam haze on right side. Note in Figs. 17 and 18 the comparatively small amount of talus thrown down by the fault movements. (Photo. by C. N. F., 1923.)

the dome that indications of fault movements may be seen, and the throw does not appear to be great. All this applies to faults in the pumiceous deposits, and therefore refers to movements which occurred near or after the close of eruptive activity. A great quantity of material was ejected from Novarupta, and here, as in the wider spaces of the valley, the settling around the vent seems referable to a collapse of the roof over the body of magma.

At the summit of Novarupta dome a wide and deep trough in the jagged lava may be due to the same cause. All these displace-

ments probably occurred very soon after the eruption. There is evidence that at present and at least for a number of years a condition of repose has prevailed. In 1919 a highly unstable-looking cliff of lava was observed on the southern side. In 1923 it was still standing and its appearance was the same as before. Many other rock masses in the dome appear ready to crash down with the slightest shock. The blocks of talus are so easily set in motion that only in a few places does it seem safe to ascend to the summit, and in these places much caution must be used.

UNLIKELIHOOD THAT DISTURBANCES IN THE VALLEY WERE DUE TO OTHER CAUSES THAN THE INTRUSION OF A SILL

In the discussion of the eruptions in the valley and the fracturing and faulting associated with them, little consideration has so far been given in this article to the possibility of their having been caused in some other manner than by the intrusion of a sill or batholith. To one on the ground any explanation which does not assign an important rôle to a body of intruded magma at moderate depth appears very unlikely. The batholithic hypothesis has been discussed; a few words should be said with regard to other possibilities.

Any such alternative explanation encounters the great difficulty of accounting in a satisfactory manner for the very close relation of the fractures to the valley area: their abundant distribution within this area and their abrupt cessation at the sides. Perhaps the least unlikely expression of such an alternative explanation would be the supposition that the valley is an old fault block, which experienced renewed dislocation at this time, with uprise of lava from a deep-lying reservoir. No evidence that the valley originated in this way has been seen, and the hypothesis does not seem to account satisfactorily for the uniform settling that it experienced in 1912. Much more irregularity of dislocation might be expected from such causes. The greatest obstacle to accepting this explanation, however, is that a tectonic movement, reaching to great depths and involving great masses of material, is implied, and the seismographic evidence fails to support this.

It may be contended that our knowledge of volcanic phenomena and their causes is not yet sufficiently exact but that there is a possibility of processes of which we have little inkling. There is some

basis for such a contention, but the idea should not be carried too far. For instance, it is difficult to picture in a wholly satisfactory manner the processes by which either a far-extending sill or dike is intruded, but there can be no question that such intrusions occur. Likewise, there is still much difference of opinion on fundamental points regarding the emplacement of batholiths, but there is no hesitation in accepting the reality of their intrusion. With reference to the valley, the sill hypothesis is not demonstrable, and a dogmatic attitude that would reject other possibilities would be unwise, but it seems to explain the phenomena more satisfactorily than any other hypothesis that has been suggested.

SUMMARY

At the time of the eruption of Mount Katmai, numerous earthquakes occurred in the surrounding region, some of which were felt as distinct shocks at points 100 miles or more from the volcano. In Part I of this article an inquiry is made as to the nature of the movements, especially as to whether they should be classed as volcanic earthquakes, due directly to the volcanic disturbances, or whether they had a deep-seated origin and should therefore be considered tectonic earthquakes.

The characteristics of the two classes are well known and are distinctive. Volcanic earthquakes are characterized especially by rapid diminution of intensity with distance from the focus; therefore a shock recognized as of considerable severity at a distance of 50 or 100 miles should have been of extreme violence in the region immediately adjacent to the epicenter, and should have produced effects recognizable several years later. During the two visits made to the region the terrain was studied for evidence relating to this matter, and the phenomena found seemed to be inconsistent with very violent movements. In many places cliffs were observed, with masses of loosely hanging rocks or insecurely supported columns, which should have been easily thrown down by movements of the severity apparently called for if the shocks felt at a distance were of volcanic origin with Katmai as the center of disturbance. On the other hand, the occurrence of a number of rock slides showed, as might have been expected, that movements of some severity, at least, were not lacking. On the whole, the evidence indicated that

disturbances occurred in the Katmai region, but they were not of extreme violence, and in order to account for all the phenomena tectonic quakes seemed to be demanded in addition to the volcanic quakes that doubtless occurred.

To confirm this tentative inference, a study of the records of seismographic stations has been made. These show, beyond doubt, that tectonic earthquakes were registered at stations over the whole Northern Hemisphere at the time of the eruption, with calculated epicenters falling as close to the Katmai region as calculations of epicentral positions usually give. The conclusion is well supported, therefore, that the eruption was accompanied by tectonic movements. It is only rarely that eruptions, either large or small, have this association, but instances are known.

In Part II, the fissures and faults produced by the outburst of the sand-flow in the Valley of Ten Thousand Smokes are described and discussed. Their most striking feature is their abundance over the valley floor and, generally speaking, their restriction to this depression. The inference is that the forces producing the fracturing were situated close enough to the surface so that surface features exercised control. Since the fissures formed vents for the extrusion of the body of pyroclastic tuff that formed the sand-flow, and later became fumarolic orifices, the presence of a body of magma at a rather shallow depth is inferred, and to this intrusion the forces of fracturing are ascribed. The question of the form and volume of the intruded body are considered, and evidence on the matter is supplied by the character of the faulting and by other phenomena.

Only two possibilities seem to require detailed consideration. One is that a sill-like body of not great thickness was intruded between the horizontal strata beneath the valley, and the other is that the valley is underlain by a batholith extending downward to a great depth.

Opposed to the hypothesis of a batholith are several considerations. The valley floor has been thoroughly fractured, and the areas of fracturing completely surround several eminences rising to considerable heights above the floor. If the whole area was underlain by a batholith close to the surface, the various blocks were left virtually unsupported except by flotation, and great readjustment

of level should have taken place to conform to this condition. It is obvious from the topographic aspect that nothing of this sort has occurred.

With a sill, on the other hand, the intrusion is inferred to have advanced under the low areas, causing upheaval of the roof, but with its progress checked when the areas underlying heavily loaded mountain blocks were encountered. With the escape of a portion of the magma through the fissures a partial subsidence followed. The deposit of extruded tuff itself conceals part of the evidence regarding the nature of the movements, but as much of the record as is visible is in accordance with expectation. The high sand-mark forms an especially important clue. This feature shows that at the time of extrusion the level of the tuff surface in the valley area was about 200 feet higher than at present. After the extrusion the floor collapsed, with an opening up of fissures following the margin of the high sand-mark, and with a down-tilting of blocks between the marginal fissures and the flat portion of the floor.

A very perceptible diminution in the temperature and volume of fumarolic vapors has taken place between the two visits of 1919 and 1923, and this adds further confirmation to the idea that the source of the emanations is a comparatively small body of igneous rock, rather than one of batholithic magnitude.

The possibility that the fracturing in the Valley of Ten Thousand Smokes might have been the cause of the tectonic earthquakes has been investigated. This supposition is shown to be untenable because the period at which the fractures must have been formed was not the period during which earthquakes were recorded at distant stations.[1]

WASHINGTON, D. C.
May, 1924

[1] Attention should be called to an article by E. Tams (Erdbeben und Ausbruch des Katmai im Jahre 1912; *Zeitschr. für Vulkanologie*, Bd. VII, Heft 3,, pp. 137–49, October, 1924) which has appeared since the present paper was written and in the hands of the editor. The main subject of Mr. Tams's article is the coincidence of tectonic earthquakes with the Katmai eruption, and on this his conclusions are altogether in accord with mine. He, however, correlates these tectonic earthquakes, in part at least, with the fracturing in the Valley of Ten Thousand Smokes. This is hardly surprising, as he, of course, had not visited the region and appears not to have seen articles relating to it which have been published within the last few years. The reasons for favoring another interpretation are set forth in the present paper.

THE BEARING OF SOME REMARKABLE POTHOLES ON THE EARLY PLEISTOCENE GLACIATION OF THE FRONT RANGE, COLORADO

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ABSTRACT

The eastern flank of the Front Range in north central Colorado shows a remarkable series of potholes related to the early Pleistocene glaciation of the region.

The areas concerned are deeply and thickly pitted with thousands of glacially carved potholes. The bearing of these ancient potholes on the condition of the ice during their formation indicates unusual features of crevassing and surface ablation.

The potholes are directly linked up with ancient cirques, U-shaped valleys, striae, and perched bowlders in the chain of evidence which indicates that these early Pleistocene glaciers covered 75 to 80 per cent of the region and had many of the characteristics of an ice cap with pendant valley glaciers, fringing well out to the foothills.

INTRODUCTION

The area under discussion is in north central Colorado on the eastern flank of the Front Range. It extends from the Continental Divide on the west to the foothills on the east, and from the North St. Vrain on the south, northward to about 40° 30′ north latitude. Most of the district is represented on the Mount Olympus and Rocky Mountain National Park quadrangles.

The field work was incidental to the study of the general geology of the region during the summers of 1921 and 1922. In addition, several weeks were spent in 1924 in the making of a detailed examination to determine the special significance of these potholes and their relation to the extent of the early ice. The area affected, although comprising about 400 square miles, is only a part of the entire region concerned, which extends north into Wyoming. Similar areas of extensive potholes are known elsewhere in Colorado.[1]

THE GLACIAL POTHOLES

The area occupied by the earliest of the Pleistocene glaciers in northern Colorado is marked, not only along the sides and floors of

[1] Personal communication from R. D. George, chief of the Colorado State Geological Survey.

high terraces along the subdued and U-shaped valleys, but over the summits of the divides, by hundreds of glacial potholes. Over one thousand of them were counted in the Estes area alone, and the total for the entire region must exceed two thousand. The potholes are always associated with ancient striae, perched bowlders, and, locally, high-terrace gravels of glacial aspect.

The glacial mills have cut mostly in the Long's Peak and Mount Olympus granites, but a few are known from the more indurated and crystalline phases of the schist and the coarse pegmatites which cut both the granites and the Big Thompson schist.[1] Locally these ice- and water-carved depressions intersect both granite and schist at the contact, irrespective of texture and foliation.

An analysis of over a thousand of the better-preserved potholes permits the following summary of their characteristics:

a) They occur in groups of six to twenty holes; solitary potholes are rare. See Figure 1. They are mostly disposed in lines, and groups of them will show a definite alignment and persistent arrangement along a given slope.

b) The individual potholes may be separate, linked together into a compound cuspate channel, or "double decked." See Figure 2. Down a steep slope, the little ones may lead into the big ones so as to make a definite plunge channel.

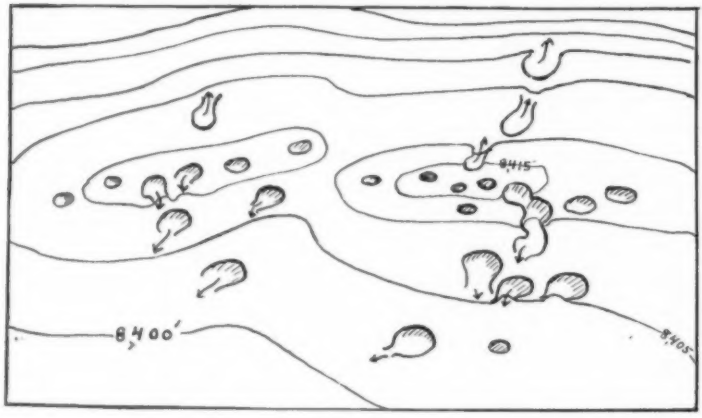
c) The holes are usually wider than deep in ratio of two to one. They are round or oval, and the oval ones show a lip-like depression at one end of the long diameter and a deeply undercut rim at the opposite edge. The floor is deeply hollowed at the undercut end and shallows at the lip. The lips invariably point down the slope of the surface in which the potholes lie. See Figure 3.

d) The potholes show a wide range of size. It is believed that the basin of Gem Lake is the largest of them, as it measures 200 feet by 150 and is about 50 feet deep at the north end and shallows to a wide lip at the south. There are two potholes at the southern end of Lily Mountain, the larger of which is over 30 feet long and 20 feet wide, with a depth of 10 feet to water level and at least as much more to

[1] For a description of the rocks of the area, see "General Features of Pre-Cambrian Structures along the Big Thompson River in Colorado," *Journal of Geology*, Vol. XXXII, pp. 49–64.

A

FIG. 1*A*.—Surface of granite boss on the slope of Prospect Mountain. The potholes show as small black dots on the surface. They are actually over a foot in diameter.



B

FIG. 1*B*.—Diagram showing a detail of *a* in contours. Note that the potholes lead into one another in channel fashion down the slope. Contour interval = 5 feet.

the algae-covered floor. The smaller one is 15 feet by 12 and proportionately deep. See Figure 4. Associated with these two huge holes are over fifty little ones ranging from 2 by 2 feet across and eighteen inches deep to tiny pits less than 2 inches across and about 1 inch deep. In the entire region, some eighty out of every hundred potholes are less than 2 feet across and from 6 to 18 inches deep.

e) The potholes are distinctly associated with elevations, i.e., the divides between the valleys rather than the valley floors. They are

FIG. 2.—Potholes and cuspate channels in granite near Gem Lake

unknown within the area covered by the latest of the Pleistocene glaciers, but occur up to and disappear under the edge of the massive moraines bordering the more recently glaciated area. They are also lacking in the "inner canyon"—the recently carved gorge varying from 50 to 100 feet in depth which has been cut by both the Big and Little Thompson rivers and their larger tributaries in the floor of the old U-shaped valleys.

f) Over 90 per cent of them are located in the summits of round, flat-topped, knoblike outcrops and bosses of granite. The remainder lie in the immediate slopes. None are known from the flat areas of the depressions between knobs. See Figure 5.

g) Not all of the granite knobs are potholed. Seen from a short distance, the profiles of the Needles, Prospect Mountain, Castle

A

FIG. 3*A*.—Pothole with a well-defined lip

B

FIG. 3*B*.—Pothole with a well-defined lip. Oval pothole with well-defined rim and wide, shallow lip.

Mountain, and many other of the lower mountains appear generally rounded and subdued, but a closer inspection reveals some detailed relief. The slopes are a series of small but distinct knobs of small elevation and varying summit area which may be 10 square feet or as much as a half-acre. These rounded and subdued bosses mount in series higher and higher to the top of the peak. Nine out of ten of these rounded masses will be pitted with the potholes, but the tenth, although in line with the elevations affected and no different from

FIG. 4.—Potholes in the summit of Lily Mountain. The larger and lower of the holes is over 30 feet at the long diameter and more than 10 feet to water level. The smaller is also oval and about 12 by 15 feet. The five small potholes on the ridge between them are all over a foot in diameter. The photograph was made about 50 paces from the rim of the largest hole and about 15 feet above it.

them in other respects, will show only a smooth and unbroken surface.

h) Gravel, except the small angular feldspar crystals loosened from the margins by weathering, is conspicuously absent from the basins of the potholes. Many of the depressions are intersected by conspicuous joints and, locally, loosened blocks have toppled downslope carrying away part of the wall of the pothole. Elsewhere the joints are the sites of chains of potholes which are linked together in step fashion down the slopes of the knobs.

In general, the appearance of the potholes is weathered and sub-

A

FIG. 5*A*.—Potholes on Prospect Mountain. These holes are characteristic of those on the summit of a knob.

B

FIG. 5*B*.—The sharply defined black spots in the summit of the rock are potholes in Little Elk Park.

dued, although many of them show a sharply angular margin, a deeply grooved lip, and a well-polished marginal floor.

The general topographic position of these depressions, their size, shape, and general alignment in connection with ice- and water-grooved surfaces points to their glacial and fluvioglacial origin.

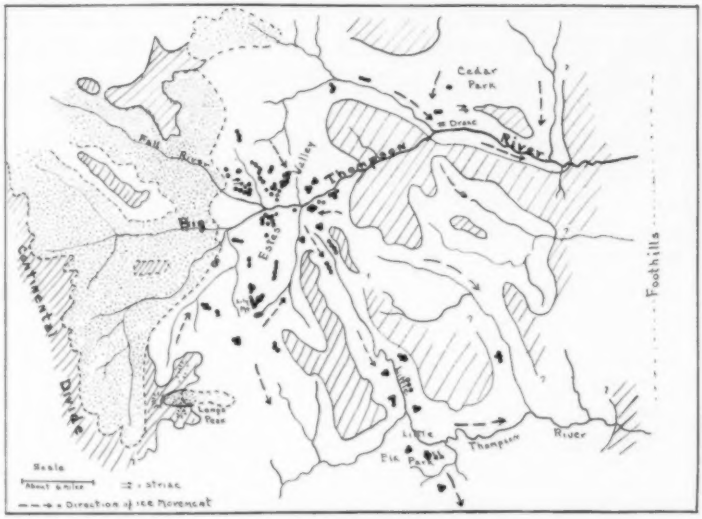


FIG. 6.—Diagram to show the areas covered by the early and late Pleistocene glaciers respectively. The areas covered by the early ice have been left uncolored, those occupied by the late ice are dotted, and the divides never occupied by glaciers are lined diagonally. The groups of black dots designate the region marked by groups of potholes.

EXTENT OF THE EARLY PLEISTOCENE GLACIERS RESPONSIBLE FOR THE POTHOLES

The boundaries of the ice were determined in the field from the evidence afforded by the potholes, U-shaped valleys, ancient cirques, perched bowlders, striae, and terrace gravels. They have been mapped as shown in Figure 6. There is little or no drift evident in connection with this glaciation.

The western border of the region occupied by the earliest of the Pleistocene glaciers lies somewhere within the region overriden by

the latest of the invasions, and is effectively masked by it. While the margins of the latest glaciers are everywhere marked by massive moraines, the edges of the area invaded by the earliest ice show no such features. It is probable that the moraines produced have long since been eroded and their débris deposited outside of the Front Range area. It is suggested that much of the material in the extensive Pleistocene mesas immediately to the east of the foothills was originally derived from this glacial drift which was dropped along the base of the mountain front by the streams which cleared the valleys.

In many places the ice of adjacent valleys was thick enough to bury their divides and submerge the crests. Around the Estes Valley striae on the Needles, Castle Mountain, Prospect Mountain, and Mounts Pisgah and Olympus, as well as the divide between the present course of the Big Thompson river and Devil's Gulch, show that the ice currents freely crossed their summits at right angles to the general trend of the elevations.

West of the Estes Valley, the ice rose to 11,500 feet on Trail Ridge, and around Park Hill it fell just short of 9,000 feet. At Little Elk Park the ice filled the valleys to over 8,000 feet A.T.

Neglecting differential warpings and allowing for postglacial erosion of the area since the ice left, evidence shows that the glaciers extended to the low altitude of 6,000 feet at Mont Rose and about 6,500 feet at Little Elk Park. Around Mount Olympus the ice must have been at least 1,000 feet thick and in the Estes Valley over 1,200 feet to surmount the summits of some of the potholed divides.

The earliest ice occupied a territory at least four times as extensive as that filled by the latest of the glaciers. From its western border at the Continental Divide it extended to within 4 miles of the foothills.

There is evidence of at least one other glacial invasion which was intermediate between the conspicuous latest glaciers and the very much earlier and more extensive earliest of the glaciers. It appears to have followed close upon the retreat of the earliest ice in a very much more restricted area. By its action the already U-shaped valleys were deepened still more, the potholes wiped out, and a

limited amount of moraine deposited. Only the most meager and limited records of this moraine are left.

The earliest of the Front Range glaciers is probably to be correlated with the sub-Aftonian or Kansan of eastern North America, while the latest is undoubtedly Wisconsin.

SIGNIFICANCE OF THE EVIDENCE INVOLVED

The amazing number of potholes, together with their positions on the summits of the knobs and bosses of granite and schist, points to unusual features of glacial drainage. It is believed that the pot-

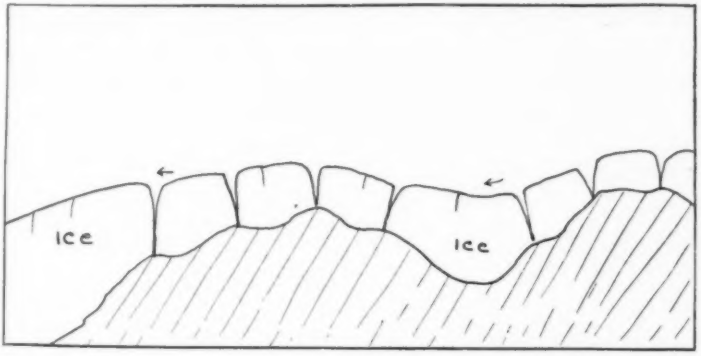


FIG. 7.—Diagram to show possible crevassing in the ice over the uneven surface of the divides around the Estes Valley.

holes mark the sites where extensive crevasses opened from the top to the bottom of the ice where it was strained across the irregularities of its bed during the later stages of the glacial occupation. It appears that the ice was practically stagnant near the end of the glacial epoch and wasted away over the entire area, so that torrents from the rapidly melting ice plunged over the walls of the numerous crevasses to the rock surface below, where they developed glacial mills and deeply grooved channels with the aid of the loose bowlders and gravel at the base of the ice.

The potholes are almost invariably along the summits of the small elevations at just the points where strain in the ice would be

most likely to cause crevassing. Where a series of potholed knobs appear, they have about the same summit elevation. From the alignment of the holes it appears that the crevasses were chiefly at right angles to the general trend of the elevations responsible for them. See Figure 7.

Had the potholes been developed by drainage at the edge of the ice, they would scarcely be located on the divides and upper walls of the valleys, but along the valley floors where the drainage was concentrated, at the edge of the low-lying parts of the receding margin. Potholes of this sort are common within the area covered

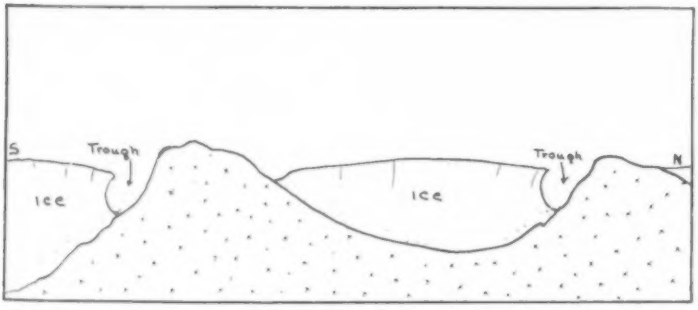


FIG. 8.—Diagram to show trough developed at contact between the glacier margin and the rock wall of the adjacent mountain.

by the latest of the Pleistocene glaciers, particularly along the course of the Fall River. Such potholes are always deeper than wide, are nearly cylindrical, and lack the lip and under-cut rim.

Some of the groups of potholes encircle the slopes of the mountains in contour fashion. It is believed that such an alignment is due to the action of waters which circulated along a trough developed at the contact between rock and ice slopes when the general thickness of the ice had lessened so that the peaks emerged as nunataks. This would be true particularly of southward-facing slopes, and it is on such slopes that "contour" potholes appear in abundance. See Figure 8.

The plateau-like "parks," as Estes Park, Little Elk Park, and

Cedar Park, including many similar areas, mark sites where numerous valley glaciers converged to erode a basin of considerable extent.

Recent exfoliation along some of the steeper slopes has scaled many of the joint blocks of the potholed knobs so that locally, as at the Needles, former bosses of granite are now reduced to pinnacles in whose summits lie scattered potholes.

SUMMARY

The extensive development of potholes in the surface of the pre-Cambrian granites and schists of the Front Range along the drainage basins of the Big and Little Thompson rivers is directly related to the crevassing and surface ablation of the earliest of the Pleistocene glaciers.

The distribution of the potholes testifies to the considerable extent of the early ice and to its considerable thickness.

THE SPOKANE FLOOD BEYOND THE CHANNELED SCABLANDS. II

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The University of Chicago

THE SPOKANE FLOOD IN COLUMBIA VALLEY BELOW THE MOUTH OF SNAKE RIVER

Wallula Gateway.—Concentration of all the Spokane discharge into one valley occurred at Wallula, where Columbia River in an antecedent course crosses a prominent upwarp of the basalt plateau, a few miles below the mouth of Snake River (Figs. 8 and 9). The canyon here has very steep walls for 750 feet above the river, and its minimum width at the top of these cliffs is a mile. This is Wallula Gateway, probably the narrowest place in Columbia Valley south of the Canadian line. Whatever its depth at the inception of the Spokane flood, the canyon was inadequate to contain the great stream. The glacial Columbia rose above the summit of the cliffs and spread westward a mile and eastward an average of more than half a mile.

The top of the western wall, for a mile back from the brink of the Gateway cliffs, is scored and channeled by a plexus of anastomosing ravines and gulches in basalt, which trend with the river course. Their gradients descend southward. At their heads they open toward the broad, low structural valley north of the uplifted tract. Southward, they lead to the brink of the broader part of the canyon below the Gateway. Erosive action has been great, for the basalt is bitten 100 to 150 feet deep in these channels. Rock basins excavated in their bottoms record great volume of water moving with considerable velocity.

And the water which traversed them did not come from higher land to the west; it came from the broad, low structural valley to the north. It entered at an altitude of 1,050 feet A.T., hundreds of feet above the bottom of that valley. The streams left the south-

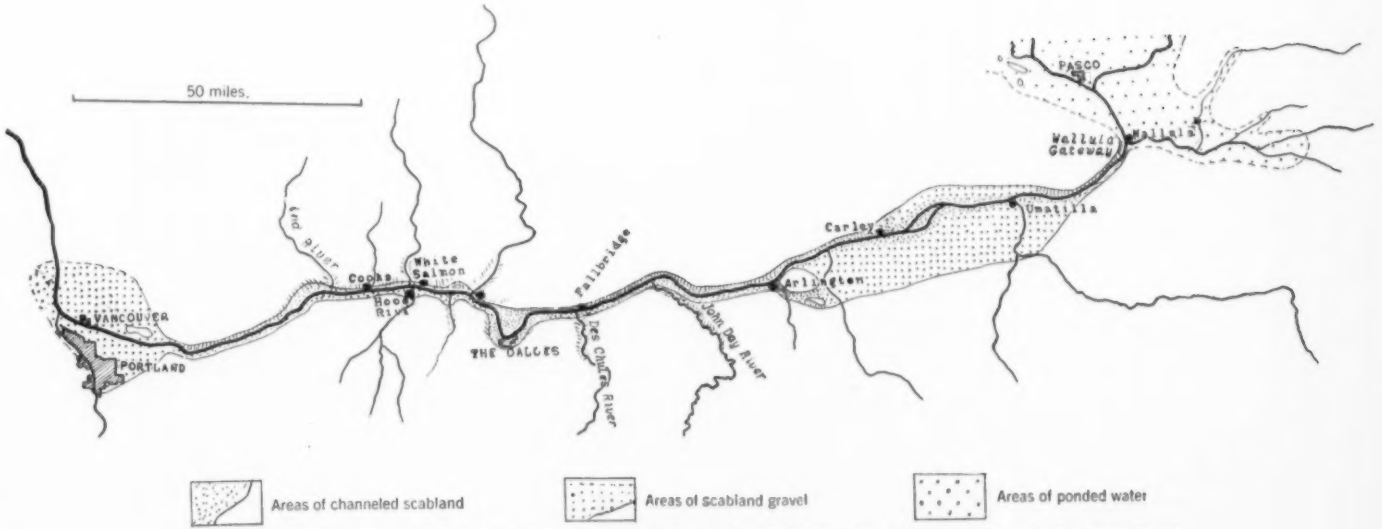

FIG. 8.—Sketch map of Columbia Valley between Wallula and Portland, showing area affected by the Spokane Flood

ern ends of these channels at altitudes of about 950 feet A.T. They did not flow down the slope to any lower level. Since they ceased to erode below an altitude of about 900, they must have entered a body of water in the broader canyon below the Gateway whose surface was not much above 950.

This is scabland on top of the western cliff of the Gateway. It is wholly unlike the topography of the higher slopes. To be typical, it needs only the bounding bluffs of loess, bar and terrace gravel, and three-fourths talus on its basalt cliffs. The steep bluffs of loess are absent, because the higher land here is all basalt. The gravel deposits are not shown, but may be present in certain rounded hillocks and shoulders. Most of the talus is higher than three-quarters, though some is typical. The basalt at this horizon breaks readily into small pieces and perhaps may have disintegrated more rapidly than the average rate.

FIG. 9.—Wallula Gateway, showing the scabland type of topography within and above the canyon walls. From the Wallula, Washington, topographic map, U.S. Geological Survey.

The east side of the Gateway has scabland up to the same level, and gentle, soil-covered slopes above. "The Sentinels" (Figs. 10 and 11) and their associated bare rock hills and channels are clearly scabland forms. And all the divides between the pre-Spokane tributary ravines which drain the higher land to the east are severely scored and notched below 1,050, so that they are separate hills instead of ridges.

Here, then, the entire Spokane flood was finally converged to make the prodigious river which filled and overflowed WallulaGateway. Here, also, was the constriction which first held up the surface of Snake and Columbia rivers, and whose enlargement allowed the

fall in their levels while the scabland rivers were running at full volume. How much widening was accomplished is not clear, but the deepening probably extended from the base of the Sentinel group of scabland buttes, 500 feet A.T., to the rock ledges in the river today at about 300 feet A.T. The increase in capacity was very rapidly produced and the backwater above the Gateway lowered early in the Spokane epoch.

FIG. 10.—The east wall of Wallula Gateway. Scabland cliffs extend about 700 feet above the Columbia. Above them, the basalt is covered with loess, and all slopes are gentle. A prominent scabland channel, shown in Figure 7, lies back among the cliffs and is not shown in this view. "The Sentinels" stand a little to the right of the center of the picture.

Estimating from the scabland above the cliffs west of the Gateway, the glacial river surface descended 50 feet or more in 3 miles. But near Snake River Junction, 25 miles upstream, the highest river-level was no greater than at the entrance to the Gateway. The cause of this is the broad structural depression in the basalt. The flood waters spread over several townships immediately north of the narrow Gateway. And in this region was deposited all gravel which had traveled with the flood through Snake River Canyon and

Columbia Valley.[1] Therefore, gravel left by the Spokane flood in Columbia Valley below Wallula Gateway must have been derived from erosion of rock ledges and cliffs also below the Gateway. In distribution and topographic expression, these deposits are unlike those in Snake River Canyon, as will appear in the following descriptions.[2]

FIG. 11.—"The Sentinels," scabland buttes in the Wallula Gateway. Talus and cliffs together are 100 feet high. Copyright G. M. Weister.

Vicinity of Umatilla.—Columbia Valley has much lower walls about 10 miles below Wallula Gateway. At Cold Springs Station, on the south side, the bluffs are not 250 feet above the river, and for 10 miles south of the Columbia here (vicinity of Stanfield [Foster] and Hermiston), the country does not rise 500 feet above the river.

[1] These deposits are now masked by eolian sand and not easily identified.

[2] The significance of the Wallula Gateway constriction was not realized when the plateau scablands were studied. The early ponding of the flood north of the Gateway must have affected the lower part of the plateau as well as the Snake and Columbia valleys. Examination of altitudes shows that lower Crab Creek Valley and Washtucna Coulee must have contained backwater from the Gateway, and that this was very probably responsible for the high water-levels which initiated Othello Channels and Devils Canyon divide crossings, and probably was a factor favoring the Drumheller Channels and Palouse Canyon crossings.

This region south of the river is largely covered with basaltic gravel deposits, disposed in broad, low hills and separated by equally broad ramifying channels which lead out of the Columbia and back again a few miles farther downstream (Fig. 12). Basalt buttes appear here and there in this area of gentle slopes. Umatilla Butte and

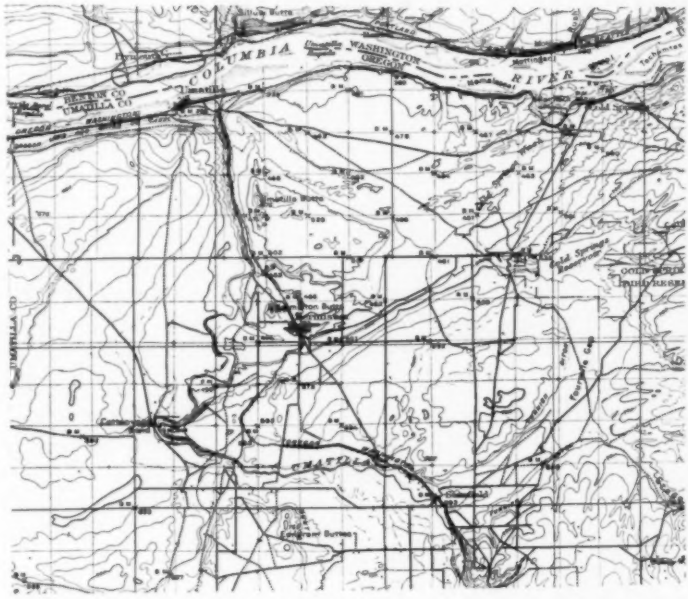

FIG. 12.—Umatilla lowland, showing braided course of the Spokane Columbia across the gravel-covered flat, and the situation of Emigrant, Hermiston, Umatilla, and Sillusi buttes. From the Umatilla, Oregon-Washington topographic map, U.S. Geological Survey.

Hermiston Butte are the most prominent ones. They, as well as the basalt bluffs of the river, are severely eroded bare rock scabland forms, and their association with the channels and gravel deposits indicates a common origin.

Both of the buttes named are due primarily to sharp local upwarp of the basalt along a north-south line. Sillusi Butte, just north of the Columbia and also on this line of deformation, is similarly

eroded on its riverward face, though wind-driven sand masks its character in part. Emigrant Buttes, 10 miles south of the Columbia, is another sharp pucker on this line, but possesses gentle slopes and a complete cover of soil. The contrast between the uneroded Emigrant Buttes and the craggy Hermiston and Umatilla buttes is very instructive. The only explanation applicable is that Hermiston and Umatilla buttes, respectively 620 and 675 feet A.T., were overrun by the Spokane flood, while Emigrant Buttes, 759 feet A.T., stood beyond and above the limits of the flood and were spared. It therefore appears that in the Umatilla lowland this flood rose nearly but not quite to 750 feet A.T. Elsewhere in the region the 700-foot contour approximately marks the upper limit of scabland and basaltic gravel.[1] A descent of about 250 feet in the surface of the Spokane Columbia therefore occurred at the beginning of the episode in about 15 miles of distance. Most of this probably occurred in the Gateway and the gorge immediately below. Certainly the walls of the canyon here bear witness to very vigorous scour for several hundred feet above the river-level. The talus on the great cliffs southeast of the river below the Gateway stands two-thirds to three-fourths the height of these cliffs. This is a good Spokane ratio; considering that post-Spokane river work probably has carried away some of the talus. The Sentinels and associated scabland knobs in the Gateway bear three-fourths talus, and therefore have not been touched by waters of the Columbia since the flood subsided. Their bases are about 200 feet above the river.

Vicinity of Carley.—There are two anticlinal folds in the basalt on the north side of Columbia River near Carley Station, both parallel to the river and both clearly expressed in the topography. Tributary streams, antecedent to the folding, have cut them into several short ridges or buttes, and, subsequent to this, the Columbia has risen high enough to flow around them all. Artesian Coulee is the most prominent erosional feature here, due largely to the flood. Its floor is so low, however, that it cannot be cited as a channel abandoned ever since the Spokane epoch. Crow Butte, anticlinal in

[1] Not all of the gravel in this lowland is of Spokane age. At Echo, Stanfield (Foster), and elsewhere are outcrops of a stained, indurated gravel with a considerable proportion of non-basaltic material. It is much older than the scabland gravel.

structure, has the scabland erosional features, though much obscured by wind-blown sand. Golgotha Butte is an isolated part of the other fold and was also surrounded. On its north side, away from the river and about 3 miles distant, is a large gravel deposit, 650 feet A.T. and 400 feet above the river. The material is unweathered and largely basaltic, but from the presence of quartzite pebbles there seems to have been incorporation of older gravel in it during the Spokane flood.

When the river was high enough to deposit this gravel, it must have spread over miles of the low country south of the river here and west of the Umatilla region. Much basaltic gravel is exposed along the railroad south of the river, but its altitude is not more than 150 feet above the river and its significance therefore slight. The low country is heavily mantled with wind-blown sand, and little is known about the material beneath. The most prominent feature is a broad flat which rises gradually westward from Umatilla River to an altitude of 650 feet and descends abruptly from this summit flat toward the west. See Fig. 12. It probably is a Spokane bar, but if so it contains a large amount of reworked material derived from the older gravel deposit below the scabland waste. There are no elevations of basalt in this low country.

Vicinity of Arlington.—The surface of the basalt rises west of Carley, and the Columbia is encanyoned thence to The Dalles, where another structural depression is entered. At Arlington, on the south side of the river and about 50 miles below Umatilla, the wall of the canyon is 850 feet above the river. On the north side here it is 1,200 feet above. The Spokane flood was confined within these walls. But there was a lower surface of the basalt, southeast of Arlington and about 6 miles south of the Columbia, constituting the broad divide between Willow Creek and Alkali Canyon, both northward-flowing tributaries to the Columbia. Overflow from the Columbia Valley backed up Willow Creek Canyon and crossed this low place to Alkali Canyon. The divide here is about 5 miles wide and nearly flat-topped (Fig. 13). On it are two distinct channels, the floors of which are about 700 feet A.T. They have much bare rock in irregular low buttes and crags, exactly like those in the scablands and along the Columbia in many places at low water. There are

numerous gravel deposits of no great magnitude on these channel floors, and a well-formed delta front with 30° slope and fine foreset bedding at the same angle extends out into Alkali Canyon at their mouths. The delta front is about 2½ miles wide, and the brink varies from 650 to 700 feet A.T.

Between Arlington and The Dalles.—Evidence for the presence of the Spokane flood is well distributed along the Columbia Valley in

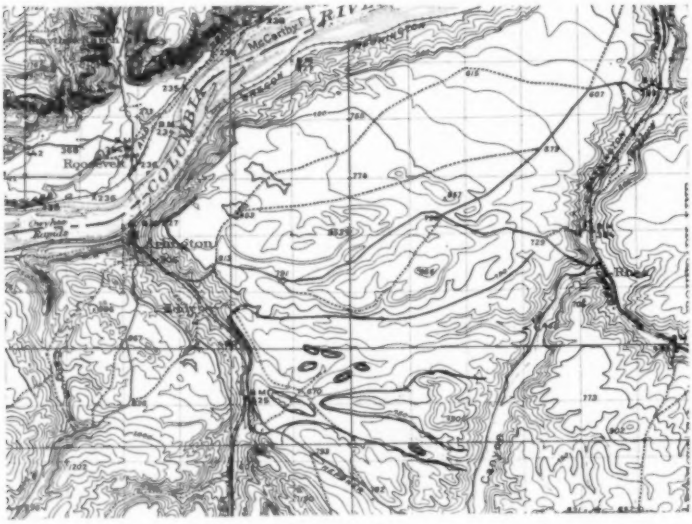

FIG. 13.—Vicinity of Arlington, showing the scabland channels between Willow Creek and Alkali Canyon and the delta front in Alkali Canyon. From the Arlington, Oregon-Washington topographic map, U.S. Geological Survey.

the 50 miles between these two towns, though there are no lowlands for records such as those at Umatilla, Carley, and Arlington. Large gravel deposits are commonly present in the mouths of tributaries whose walls at junction with the Columbia were lower than the upper surface of the flood. Salients in the Columbia's walls are strikingly cliffed, and many have secondary channels in basalt back of them where the flooded main spread. Since the character of such features is already familiar to the reader, only a list is given here, as the simplest method of indicating the weight of the evidence.

Jones Canyon, south side of Columbia, 1 mile west of Arlington. Large gravel bar with beautiful aggradational slopes descends into canyon mouth from rock shoulder on the east. Rim rock of the cliffs both east and west of the canyon mouth is scrubbed.

Lang Canyon, south side of Columbia, 4 miles west of Arlington. Large gravel bar in mouth, depending from the eastern or up-Columbia shoulder. Scabland topography on summit of rock terrace just east of bar. Upper limit of scabland 650 feet A.T.

Chapman Creek, north side of Columbia, 5 miles west of Roosevelt. Gravel terrace of basaltic débris in mouth. Summit about 600.

Blalock Canyon, south side of Columbia, 8 miles west of Arlington. No gravel deposit in mouth. Eastern wall at mouth is 950 A.T., too high for the flood to cross.

Rock Creek Valley, north side of Columbia, 13 miles west of Roosevelt. Gravel terrace on west side of mouth. Altitude about 650. Basaltic material.

Unnamed canyon, south side of Columbia, ½ mile below Rock Creek Rapids. Pronounced gravel bar in mouth.

Goodnoe Station, north side of Columbia. A well-formed gravel bar lying against the Columbia bluffs a little west of station. Not a dependent bar. Has aggradational slopes on both upstream and downstream ends.

Columbia Mountain, north side of Columbia, about 10 miles east of Maryhill Station. Lower ledges of basalt are much scrubbed and carry the "dalles," or flat-topped, steep-sided knobs and low buttes. Except along face of Columbia Mountain, the talus here is three-fourths. Eroded face of the mountain is composed of nearly vertical basalt flows, much brecciated, which crumble much more rapidly than the average. Talus covers the whole face of the great cliff.

Rufus Station, south side of Columbia. Good gravel bars depend down the Columbia Valley from salients here. Two tributary gulches, each with bars or remnants of a complete blocking in their mouths.

John Day Canyon, south side of Columbia. No gravel bar in mouth. East wall at junction with Columbia was too high.

Maryhill Station, north side of Columbia. A side-hill bar, not dependent from a salient, extends from 500 to 600 feet A.T. on the slope above the station. Face of basalt cliff between Maryhill and Fallbridge is rugose like scabland. Buttes of same character on south side of river near summit of bluffs. Also a sidehill gravel bar whose bedding dips parallel to the down-valley surface slope of the bar.

Biggs Station, south side of Columbia. Large gravel bar, like a great shoulder, partially fills mouth of canyon here. It depends from the west, or downstream, spur and points up the Columbia. An unusual but not unknown type of bar, due to an eddy in the great stream in a re-entrant of the valley walls to the lee of a prominent salient.

Des Chutes Canyon, south side of Columbia. No bar here. East wall of tributary canyon too high for flood to cross. Scabland forms along much of the

south wall of Columbia Valley between mouths of John Day and Des Chutes rivers.

Fallbridge Station, north side of Columbia. In vicinity of this station are striking basalt knobs, high, narrow, and steepsided, above the railroad level but at foot of the high bluffs. A great, butte-like island, castellated and channeled, stands here in mid-river. It is genuine scabland, identical with hundreds of such features on the plateau, except that a river still swirls past its base and its talus ratio is therefore low. Prominent rock terrace 100 feet or so above railroad bears scabland for some distance from Fallbridge downstream.

The Dalles.—This city is built in the middle of a structurally determined broad valley in the basalt. Two sedimentary formations here overlie the basalt, one older than the deformation and one younger. The lower one is a river deposit commonly known as "The Dalles Beds," and in all probability is a phase of the Satsop formation. The upper deposit, largely of volcanic débris, has never been described.

Into this structural depression the Columbia enters from the east through a series of cascades and races known as "The Dalles of the Columbia." There is no place in the Pacific Northwest today which more closely reproduces the Pleistocene scabland rivers of the plateau than do these "dalles."[1] The river races almost all the way across the depression and, on leaving it, enters the famous Gorge of the Columbia across the Cascade Range.

A large part of the low area on the north side of the river is swept clean of the sedimentary formations above the basalt and is a barren waste of black rock knobs and buttes, rock basins, gravel bars, and active dunes. So far as its character is concerned, it might have been transposed bodily from the plateau scablands. Its altitude above the Columbia is not great, however, and it has been easy to assume that the obviously stream-eroded rock flat, 10 square miles or more in area, was an abandoned portion of the valley floor, left in the ordinary course of valley-deepening by the present stream. However, the Columbia of the present is a puny stream with which to sweep this flat. Almost all of it must be covered by a stream at one time, for the tract has but little relief. Furthermore, the breaking down of the knobs and basin walls during normal valley-deepening would

[1] "The Dalles Type of River Channel," J Harlen Bretz, *Jour. Geol.*, Vol. XXXII (1924), pp. 139–49.

have obliterated the higher of these features, while those nearer present river-level would be relatively fresh, and this contrast does not exist. The open channels and holes in basalt, associated with gravel bars in the lee of knobs, indicate a volume adequate to cover the flat when they were formed.

It is significant that the weakly consolidated sedimentary deposits above the basalt have steep slopes facing this scabland at The Dalles. Though they are not as distinctive as the same features in the plateau loess, the occurrence of two or three circumdenuded hills of sediment on the upper margin of the scrubbed basalt strongly suggests the same origin. There seems to be no definite marker in the topography here for the upper limit of the flood.

Lyle.—There is probably no better-displayed bar of the Spokane flood below Wallula Gateway than the one which lies just north of the town of Lyle, Washington. Its outlines are clearly expressed, its location and relations to the shape of the valley are ideal, its structure is unequivocal, its composition is exactly what is demanded, and its altitude above the present river is adequate.

Lyle is in the Columbia Gorge, ten miles below The Dalles. Columbia River crosses an upwarp of 3,000 feet in the basalt[1] between these towns and enters at Lyle a synclinal area[2] in which its gorge has much lower walls. The Spokane flood rose above these walls and overflowed a part of the structural valley's floor. Slackened current resulted in places along the margins of the broadened river, and deposition was the consequence. The Lyle bar was one product (Fig. 14). Its summit is about 200 feet above the Columbia (precise altitude not known), its materials descend on the slope to about 50 feet above the river, its slopes are convex, it has no river cliff and almost no gullies, its structure in excavations is foreset with the dip *up* the Columbia, and its situation is in the lee of a prominent cliff of basalt. It rests against the hillside back of it, but its eastern and upstream end is a rounded ridge not in contact with the hill. Probably its débris has come in large part from the face of the cliff immediately upstream.

It cannot be interpreted as a terrace remnant of a once continuous valley fill. The case is so clear that the writer, years before he

[1] The Ortley anticline. [2] The Mosier syncline.

knew of the existence and significance of plateau scabland, was convinced from the character and setting of this deposit that it was a shore bar built in an eddy in an immensely swollen river whose bottom then was not much higher than that at present.

Another deposit of the Spokane Columbia is well shown a mile west of Lyle on the Evergreen Highway. Pits along the highway show a gravel deposit whose bedding dips *away* from the Columbia and up a small tributary valley. The upper limit of the exposures is 390 feet above Lyle, 490 feet A.T., and it extends down the slope for 200 feet. Not one pebble in a thousand is of non-basaltic material. In the gravel are large angular fragments of basalt that have

FIG. 14.—Lyle bar in lee (to the left) of cliffed salient. Foreset bedding dips toward the cliff, or up the Columbia. Photo by C. S. Reeves.

been riven off near-by cliffs, up over which the fine gravel was carried from the open Columbia. The summit of the deposit constitutes a dissected terrace 530 feet A.T., and is traceable back into a channel which re-entered the Columbia about a mile farther downstream at an altitude not much less than 530. The channel is cut in the Satsop formation, itself a gravel deposit, but there is no possibility of confusing the two gravels, for the Satsop is much dissected, is tilted with the basalt, is somewhat indurated, has no foreset bedding, is capped by a lava flow, contains a lava flow, and also contains strata of volcanic ash and pebbles of quartzite and granite.

Scrubbed basalt slopes and cliffs are prominent features on both sides of the river about Lyle. On the Washington side above Lyle the slope of the valley is soil-covered from the summit (about 2,000

A.T.) down to an altitude of about 600 feet, but below this, though the slope is about the same, are exceedingly rough, bare rock surfaces.

Water from the Spokane Columbia crossed a low place in the spur between the main gorge and the canyon of Mosier Creek on the Oregon side, west of Lyle, and carried basaltic gravel over into the tributary canyon. The deposit lies on the east side of the canyon. Its material is fine subangular gravel, like that at and near Lyle, and it has foreset bedding which dips away from the Columbia and this notch and into Mosier Creek Valley. Its altitude is about 450 feet A.T., more than 350 feet above the surface of the Columbia.

Vicinity of Hood River, Oregon.—The Columbia crosses another anticline west of Mosier[1] and enters another synclinal valley at Hood River and White Salmon. On the south side of the deep gorge in this upfold are castellated crags and ridges paralleling the river, with linear channels in basalt separating them from the main hillside. The Columbia River Highway traverses some of these channels whose floors are at least 400 feet above tide. The crags are as severely eroded on the side toward the hill as they are on the river side, and talus about three-fourths the height of the cliffs flanks them in the abandoned high channels. They are as clear a record of erosion by the Spokane Columbia as anything in the Gorge.

Grading in the serpentine curves of Columbia River Highway on the east side of Hood River Valley has exposed a great deal of fresh subangular basaltic gravel up to 300 feet A.T. It lies just where a deposit should lie if the crags and channels were eroded by a greatly swollen stream.

In the southwest part of the city of Hood River is a gravel terrace 500 feet A.T. In it is a large pit at about 450. The deposit is like that elsewhere associated with the scabland flood in the Columbia Valley, except that it has a flat top and its structure consists of the ordinary current type of foreset laminae in horizontal strata. No long delta foreset structure was seen. Up to the same altitude for 3 miles or so west of Hood River are many large rolled bowlders of the underlying Herman Creek lava. Above this level, the orchard land is soil-covered, unterraced and unbroken by outcrops of rock,

[1] The Bingen anticline.

and without any bowlders. If it were not for features at White Salmon, shortly to be described, this would be taken for the upper limit of the flood.

At Columbia Gorge Hotel, west of Hood River a few miles and on the brink of the 200-foot cliffs of the Columbia, is a typical scabland expression of knobs and channels in the Herman Creek lava, and, in addition, a feature nowhere found in the Columbia basalt scabland—potholes! The worn surfaces are undeniably of this genesis, though their outlines record the onward sweep of river-borne débris, rather than the drilling in minor eddies or in cascades.

White Salmon, Washington.—The highest and largest deposit made in the Columbia Gorge during the Spokane flood underlies this town, directly across from Hood River. It is a great eddy bar, situated almost exactly as is the Lyle bar. Its material contains 90 to 95 per cent of Columbia basalt débris. The texture is fine enough for highway surfacing, though here and there are angular fragments of basalt a foot or so in diameter. Foreset delta bedding or foreset laminae in horizontal or gently inclined strata show in every cut. And, without exception, all of the many exposures show a dip up the Columbia or back into the tributary valley here or some component of the two. The summit altitude is the astonishing figure of 670 feet A.T.

The great bar depends up the Columbia Valley from White Salmon Butte. Its summit is highest at the base of the butte and is progressively lower, and its width progressively less, toward the east. It is 330 feet A.T. at the eastern terminus. It lies on a rock surface which slopes in the same direction, so that its thickness is nowhere the difference between the upper and lower limits.

The bar seems to be compound, a lower and longer bar lying on the riverward face of an older, higher bar. The summit of the lower is 600 feet A.T. Its eastern terminus originally blocked the tributary valley here. In the ravine subsequently cut through this tip, the foreset bedding is very well shown (Fig. 15). It is of the delta type and dips toward the back side of the bar, not along its length. The back slope (the slope away from the Columbia) parallels this bedding. The top and the front slope truncate it. Depth of the exposure is about 40 feet.

Cooks, Washington.—A gravel deposit along the Evergreen Highway east of this town has a terrace-like top 310 feet A.T. It lies on the west side of the mouth of the tributary Little White Salmon Valley. The north wall of the Columbia Valley here for 6 miles upstream is composed almost entirely of the Underwood lava, much younger than the Columbia basalt. 80 to 90 per cent of the material in the gravel deposit is of Columbia basalt, with Underwood lava ranking next in abundance.

FIG. 15.—White Salmon bar. Section in back slope near lower terminus, showing the foreset bedding, which dips away from the Columbia.

Foreset beds dip toward, and downstream along, the Columbia cliffs here. Large irregular blocks of Columbia basalt and large rolled pebbles of Underwood lava occur in the gravel, which otherwise is fine enough to put directly on the automobile highway. The riverward slope truncates the foreset bedding and carries the large pebbles of Underwood lava. Unless the deposit originally extended completely across the mouth of the Little White Salmon from the cliffs of Underwood lava, these pebbles must have been rolled up the slope something like 200 feet to come to their present position. The whole deposit lies on, and to the downstream side of, scabland knobs of Columbia basalt.

Mouth of Wind River, Washington.—Along the Evergreen Highway west of the bridge across this river is an excellent exposure of coarse sand and very fine gravel, 150 feet thick, which belongs to this category of deposits of the Spokane flood. It is much cross-bedded and has considerable long foreset bedding which dips away from the Columbia and up Wind River Canyon. The upper limit is 400 feet or more A.T. East of the mouth of Wind River perhaps a mile is another exposure of this material at 350 feet A.T. The upper limit here is 440 feet above the sea.

THE PORTLAND DELTA

Though the foregoing description of the effects of the Spokane flood in Columbia Valley below Wallula is not complete, it includes the more significant features now known. If it be granted that the observer has had an adequate training and that his field study has been sufficiently extensive and discriminating, it must be admitted that the existence of a great flood in the Columbia, transcending any known similar phenomenon, has been established. But the story is not complete until this vast river has been traced to its debouchure. To a consideration of this we now turn.

The debouchure of the Spokane Columbia was in the Williamette structural valley, between the Cascade and Coast ranges. Here it entered an estuary of the Pacific whose surface stood more than 350 feet above present sea-level. Here it built the Portland Delta, of which 150 square miles still remain. More than 50 square miles have been removed by the Columbia and Willamette rivers since it was deposited. The delta apparently never grew more than 8 or 10 miles beyond Vancouver.

The Portland Delta is a subaqueous deposit, an affair of river-bottom deposition, and was not a delta plain when constructed. The river was 100 feet deep over much of the surface when it was built. The evidence for this conclusion is developed in the following description.

The gravel of the delta is predominantly of basalt. It is unweathered except at the very surface, where there is some discoloration, and is easily distinguishable from the Satsop gravel, also widely exposed in this valley. Its structure is shown in hundreds of ex-

posures throughout a vertical range of 350 feet. In almost every one, the gravel is delta foreset. The dip is dominantly southwestward in the southwestern part of the area covered, westward in the central part, and northwestward in the northwestern part.

The surface of the delta lies largely in two levels, about 200 and about 300 feet A.T. In some places the slope between the two levels is gentle, but in most places it is steep. The 300-foot level occurs in isolated portions. Some of these lie against higher land along the northern and southern sides of the delta, some occur in the lee of eminences of older rock which rose above the surface of the flood, and some constitute narrow ridges on the 200-foot level elongated with the direction of stream flow when the delta was made. Excepting only in the immediate vicinity of Columbia and Williamette rivers, the original surface of the great gravel deposit has been altered by erosion only to an insignificant degree. The land forms on it are constructional.

An earlier interpretation of the Portland Delta[1] considered the 200-foot level as the result of dissection of an originally continuous 300-foot plain. This view becomes untenable when the ridges on the 200-foot level are carefully studied. Most of these ridges are grouped in the vicinity of Hidden Station, 4 miles northeast of Vancouver. They are long, narrow, and straight. The most striking one is $1\frac{1}{2}$ miles in length and about 300 feet wide on top. They stand from 50 to 100 feet above the swales which separate them. Those which appear wide on the map (Fig. 16) are closely placed parallel groups, partially coalesced. They are composed of foreset-bedded sand and very fine gravel, 95 per cent basalt. The foreset bedding, so far as shown, dips down the northern slopes in parallelism with those slopes, and is truncated by the tops and the southern slopes. The swales among these ridges contain lakelets and swamps elongated with the ridges. There are no streams in them, and no ravines lead from them to the nearby Columbia. The ridges have an orientation approximately radial to the curved edge of the delta. This

[1] "The Late Pleistocene Submergence in the Columbia Valley of Oregon and Washington," J H. Bretz, *Jour. Geol.*, Vol. XXVII (1919), pp. 502–3. In this paper the age of the delta was considered as Wisconsin. Since the paper was written, the scabland history has been deciphered, and the delta is seen to be a product of the Spokane flood, not the Wisconsin submergence.

gives them a northwestward divergence. The northernmost are composed only of sand. In form they closely resemble eskers, but they lie 75 miles south of the limit reached by the continental ice, and their field relations clearly prove them to be parts of the delta.

These ridges are held to be river bars, standing about 100 feet above the main channel floors. A stream of at least that depth thus must have spread over the 200-foot level of the delta while it was

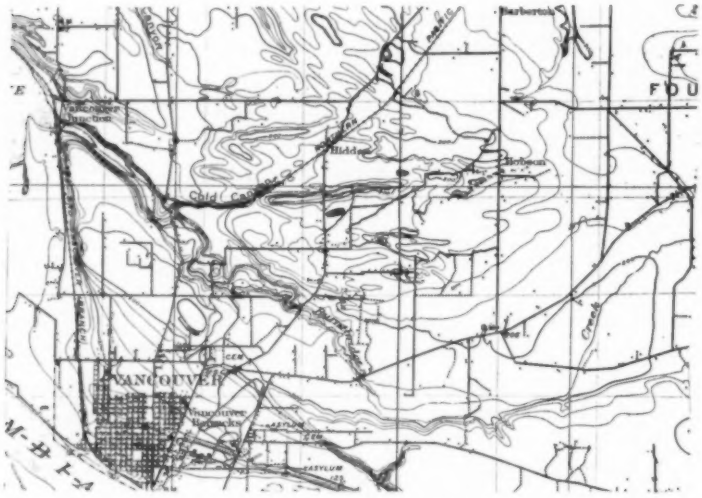

FIG. 16.—Part of the Portland Delta, showing portions of the 200-foot and 300-foot levels and the group of narrow linear bars about Hidden Station. From the Portland, Oregon-Washington topographic map, U.S. Geological Survey.

being built. Admittedly, this interpretation would be difficult to establish without other evidence for the depth of the river. Another feature of the delta, however, throws light on the question. It is Rocky Butte and the delta surface in its proximity.

Rocky Butte.—Rocky Butte (Fig. 17), in the northeast part of Portland, is a hill of basalt nearly surrounded by the Portland Delta. Its lower slopes are cliffed on the east and north, and from its northern base the land descends to the flood plain of the Columbia. The delta surface east of the butte is 300 feet A.T., but between it and

the cliffed face of the butte is a fosse whose floor is not far from 125 feet A.T. At the bottom is a closed depression more than 1 mile long, less than ½ mile wide, and averaging 20 to 25 feet deep. At the north the fosse opens toward the Columbia. At the south it widens and divides into two long arms, one extending west and one southwest.

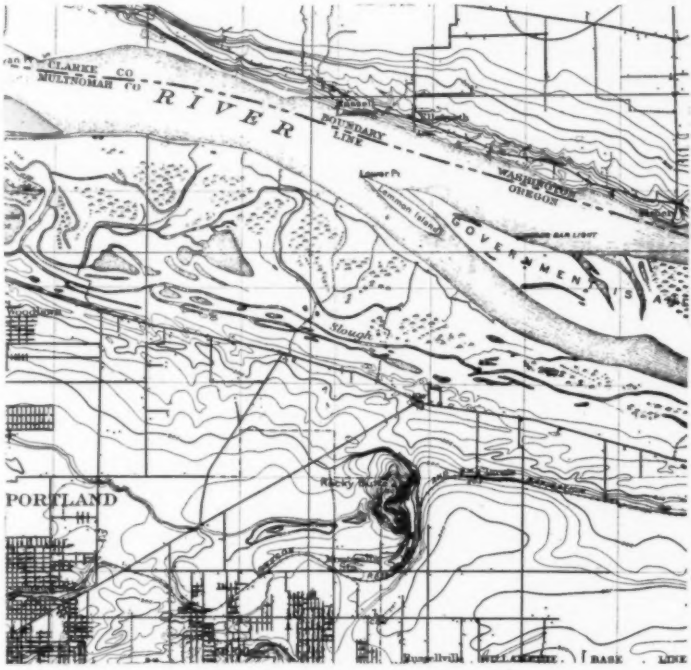

FIG. 17.—Part of the Portland Delta, showing Rocky Butte and environs. From the Portland, Oregon-Washington topographic map, U.S. Geological Survey.

Its floor gradually rises also, the trench-like character disappears, and it blends into the delta surface at about 225 feet A.T.

Abutting against the rock hill on the west is a terrace exceeding 250 feet in altitude. This terrace is much elongated and extends westward for about 9 miles, its summit descending below 150 feet in this distance. On the south, the terrace is bounded by a steep

slope which, for $1\frac{1}{2}$ miles west of the butte, has an elongated depression at the base.

What is the explanation of these features at Rocky Butte? It is easy to say that Columbia River produced them, and probably no one would object to this assignment of responsibility. But the situation demands something more than the river at a higher level. The water that flowed southward through the fosse at the east foot of Rocky Butte had to rise from below 125 feet to above 225 feet. It therefore was more than 100 feet deep in the fosse. Even then, it is difficult to conceive of the narrow fosse as erosional in origin.

But if we postulate a flood of proportions sufficient to cover the entire surface of the delta, the whole situation becomes clear. The fosse is but the unfilled locus of an eddy caused by downward deflection where the current impinged on the east face of the butte. The lower cliffed portion of the butte is the product of the same eddy. The 300-foot terrace east of the fosse never was, never could have been, extended to reach Rocky Butte. The dependent terrace to the west was deposited in the slack water below the obstruction. All parts and all levels of the delta here were formed at the same time. The velocity of the water alone determined the height to which the subaqueous parts of the deposit grew. Exactly similar situations are seen in all streams with traction loads and mid-current obstructions of sufficient magnitude.

The highest known portion of the delta is a broad eddy bar in the lee of the southern shoulder at the mouth of the Gorge. It lies between Troutdale and Gresham, and its highest part reaches 363 feet A.T. All of it is above 325. Exposed in its eastern part is the familiar dark basalt gravel, foreset-bedded with dip up the Columbia, as all lateral eddy bars should have. Some of the foreset beds at the east end of the bar dip northward, recording the return current of the eddy, moving back into the main flood. West of this bar is a broad channel floor about 100 feet lower, and still farther west is the 300-foot portion which lies east of Rocky Butte. The butte stands 8 miles out on the delta from the mouth of the Gorge.

The eddy bar south of Troutdale is 50 miles down the Columbia from White Salmon. The difference in altitude between the Spokane gravel deposits at these two places is 300 feet. The valley in this

distance has no noteworthy constrictions to which this difference in altitude could be ascribed, as in the case of Wallula Gateway. The river never had any such surface gradient as 60 feet to the mile in a broad, open valley. Further, the White Salmon bar is higher than any known deposits of the flood for 100 miles upstream. If these bars and the delta are contemporaneous, the superior altitude of the White Salmon deposit apparently must be attributed to post-Spokane differential uplift in the vicinity of that town. But bars and subaqueous delta forms do not record the surface of the water in which they were deposited. It is difficult, if not impossible, to ascertain definitely the upper limit of the flood below the loess-covered plateau. Because of this difficulty and because of the absence of direct field evidence for differential movement, the writer hesitates to build such items into his explanation of the Spokane flood.

THE VOLUME OF THE FLOOD

If the volume of the Spokane flood can be measured anywhere, it can be measured at Wallula Gateway. Certain assumptions must be made, however, as to the capacity of that notch at the inception of the flood. The platform on which "The Sentinels" stand appears to be a remnant of the pre-Spokane floor at about 500 feet A.T. Spring Gulch is a hanging tributary valley which enters the Columbia just below the Gateway. The abrupt steepening of gradient in it occurs at close to the same altitude. The position of "The Sentinels" indicates that the pre-Spokane width of the notch did not exceed $\frac{3}{4}$ mile.

The waters rose to about 1,025 feet A.T. in mid-length of the Gateway, and had a surface gradient through the Gateway of about 15 feet to the mile. A cross-sectional area of the flood at its inception, to include that which spread back on the summits of the cliffs, amounts to approximately 3,485,000 square feet. The surface of the flood descended to 775 feet A.T. at the mouth of Juniper Canyon, about $8\frac{1}{2}$ miles below mid-length of the Gateway, and its cross-sectional area there appears to have been about 2,006,000 square feet.

These figures have been used by Mr. D. F. Higgins, of the University of Chicago, as a basis for computing the volume of the initial

flood before any noteworthy deepening or widening had lowered its surface. Mr. Higgins used Chezy's formula $v = c\sqrt{rs}$, in which v is velocity, r the hydraulic radius (area of section divided by wetted perimeter of same), s the slope of the surface (expressed as tangent of angle of slope), and c is a constant. The value of c depends on the character of the channel, and was chosen to indicate a maximum of impedance from irregularities of sides and from eddies and cross-currents generated by turns in the course of the valley. This formula was devised for and is applied to small-capacity drainage lines, such as sewers, ditches, etc., and its use here involves the assumption, which cannot be true, that conditions in this enormous river were similar. However, it is the nearest approach to any formula which can be used. The actual volume probably was greater than the computed one secured by its use.

On the basis of surface slopes, the velocities indicated are 20.6 feet per second for the current in the Gateway itself and 30.4 feet per second for the current just below Juniper Canyon. On the basis of cross-sectional areas, the velocities appear as 17.5 feet per second in the Gateway and 35.7 feet per second at Juniper Canyon. Using mean velocities and computing for discharge (area × velocity), the enormous quantity of 66,132,000 second-feet, or 38.9 cubic miles per day, is secured. As above noted, this figure is probably below the actual amount. As it stands, it represents the melting of about .42 cubic miles of ice daily. The maximum measured flood of the Columbia at The Dalles, 100 miles downstream, is 1,170,000 second-feet. The Spokane flood thus was much more than 50 times the volume of present-day floods in the Columbia.

Another quantity of importance in interpreting the Spokane flood is the area of ice which, by surface ablation, could yield this prodigious quantity of water. Using the average maximum summer solar radiation of Lincoln, Nebraska, and Madison, Wisconsin (about 500 calories per square centimeter), Mr. Higgins finds that a maximum depth of summer melting by direct insolation today would be 2.66 inches. At this rate of melting, approximately 1,000,000 square miles of ice would be required to yield the water for the Spokane flood. But if the drainage of the Cordilleran ice sheet was controlled by the existing major divides and river valleys, not

100,000 square miles could have contributed to the discharge which crossed the Columbia Plateau. Obviously, the rate of melting must have been far greater than any direct insolation could have produced.

Computations such as these strongly incline one to doubt the actual occurrence of the flood. The writer has repeatedly been driven to this position of doubt, only to be forced by reconsideration of the field evidence to use again the conception of enormous volume. It is the only adequate explanation of the phenomena. These remarkable records of running water on the Columbia Plateau and in the valleys of Snake and Columbia rivers cannot be interpreted in terms of ordinary river action and ordinary valley development. The factors of declivity, of valley shapes, of rock, and of time cannot be adjusted to explain them. Enormous volume, existing for a very short time, alone will account for their existence. The field evidence all the way from Spokane to Portland, a distance of 300 miles, knits together in a consistent whole to support this explanation. Though there are a few features of the record whose origin is not yet understood, none are known which weaken the hypothesis.

FINAL STATEMENT

That the Spokane flood occurred is clear. That it was short-lived and waned very promptly after diversion around the northern margin of the plateau seems probable. The exceptional conditions which caused it are still obscure. All phases of glacial behavior considered, the writer at present can conceive of only two possible explanations for this flood. One is a very rapid and short-lived climatic amelioration in which warm winds and warm rains produced great surface ablation of a much-fissured ice sheet before the front of the ice retreated from the northern margin of the plateau. Apparently no such climatic change is recorded elsewhere, and the rapidity demanded seems impossible of realization.

The other possible explanation is that the Spokane flood was a gigantic "jökulloup," such as have occurred in Iceland repeatedly when volcanic activity has broken out beneath the cover of an ice cap. But nothing has been found in the literature to suggest Pleistocene vulcanism in the area which was drained across the Columbia Plateau during this episode.

CHINK-FACETING: A NEW PROCESS OF PEBBLE-SHAPING[1]

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ABSTRACT

Chink-faceting is the name here applied for the first time to the localized grinding of facets on the surfaces of pebbles and cobbles which are lodged in chinks of various shapes and sizes on rocky beaches. The pebbles are lodged in these crevices in such a way that they are free to move to and fro to a slight extent, but not to escape, under the continual action of the waves. The process takes place both between the bowlders of a stable bowlder beach and in cracks and grooves of the bedrock of projecting headlands, and develops pebbles of distinctive form.

Chink-faceted pebbles were first found by the writer in January, 1924, on the south coast of West Molokai and at Halawa on the east end of the same island. Later in the same year pebbles and cobbles of this sort were noted at a number of localities on the south and west coasts of the island of Lanai and elsewhere as indicated in the tabular summary (Table I). At all these places the pebbles were found in place in the site of formation and made possible the study of the process as well as the products.

TABLE I

CHINK-FACETING LOCALITIES IN CERTAIN ISLANDS OF HAWAII

Number	Island	Coast	Locality	Latitude	Longitude
1420	Molokai	South	Keawa Kalani	.....	157° 18′
1772	Molokai	East	Kalawa	21° 10′	.....
2097	Lanai	West	Kaumalapau	20° 48′	.....
2140	Lanai	South	Kealiakapu	.....	156° 58′
2141	Lanai	South	Kealiakapu	.....	156° 58′
2202	Lanai	West	Kaumalapau	20° 48′	.....
2293	Lanai	West	Kaumalapau	20° 47′	.....

Since the pebbles found at the two localities on Molokai may be regarded as the type specimens of their kind, several of them will be described specifically, as will also one from Kaumalapau, Lanai.

[1] Published with the permission of the Director of Bishop Museum, Honolulu, T.H.

Number 1420A.—This is a pebble of dark-gray, fine-grained basalt which measures 82 by 70 by 45 millimeters. One side of the pebble is rounded, and the other has a rooflike form with a sharp crest running for a distance of about 30 millimeters between two rounded points that lie at the extreme ends. About 75 per cent of the surface of the pebble is moderately smooth but not polished. The rest of the surface is made up of about twenty[1] facets having a smoothness amounting practically to a polish. The largest of these is 35 by 16 millimeters, the smallest 6 by 5 millimeters. These and

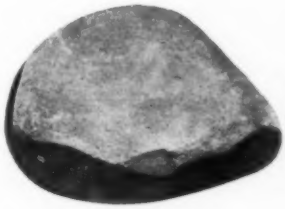

FIG. 1

FIG. 2

FIG. 1.—Chink-faceted pebble 1420*A*. Length 82 millimeters. Note the extreme sharpness of the boundaries of the small facet at the front and its longitudinal concavity.

FIG. 2.—Chink-faceted pebble 1420*B*. Length 115 millimeters. Note the faint groove-like striations on the facet at the left.

many of the others have sharply defined edges; some are less well defined and merge into the normal surface of the pebble. This pebble apparently occupied several positions successively in acquiring the facets it now carries.

Number 1420B.—This cobble is 115 by 90 by 75 millimeters and is composed of moderately fine-grained light-olivine basalt porphyry. The transverse cross-section is triangular, but as a whole it would be classed as subrounded. Fully one-half of the entire surface is contained in at least twenty smooth facets. The largest of these makes up the whole of one of the faces of the triangular prismoid and is 95 by 70 millimeters. The smallest facet is about 10 millimeters in

[1] The number is in doubt, chiefly because of the difficulty in deciding whether certain of the facets shall be called single units or divided into several.

diameter. So many of the facets of this cobble meet at very slight angles and still very distinctly that it seems probable it was formed at different stages by slight rearrangements in the same crevice.

Number 1772A.—This is a pebble of medium-gray porphyritic basalt. The pebble is 65 by 50 by 40 millimeters and has a rather rough general surface of subrounded form. Perhaps 35 per cent of the surface is occupied by about nine principal facets, which are distinctly smoother than the rest of the surface. The most remarkable facet on this pebble is concave, 35 by 18 millimeters and with a depth of 4 millimeters. Two other facets show a compound "chattered" surface not unlike that produced by dressing a broad area of wood with a small gouge, or the markings of a beaver's teeth on the tree he has felled. These surfaces appear to be the result of abrasion by the point of a movable adjacent pebble which was subject to a small amount of change from time to time.

FIG. 3.—Chink-faceted block from location 2293. (Not the same as the one described in the text.)

Number 1772B.—This is the largest chink-faceted cobble collected, and is composed of light-gray, moderately vesicular basalt. It is 260 by 170 by 100 millimeters, and about half its surface is somewhat rough with a growth of barnacles and other calcareous organisms, the remaining half of the surface being made up of some sixteen facets, which are much smoother than the rest of the cobble surface. The largest of these facets makes up the larger part of one of the sides of the cobble. There are several edges formed by the meeting of two facets which have a length of ten centimeters or more. The bulk of the facets are 3 or 4 centimeters long by half as broad.

Number 2293.—A cobble of fine-grained vesicular light-gray basalt 190 by 120 by 80 millimeters. The form is very irregular and subangular. Viewed from every possible direction, the profile shows

at least two important re-entrants, and there are five prominent projecting points flanked by concave portions of the surface. Several of the saddle-like concave edges of the cobble carry smooth chink-facets, and other facets are developed across the sides and ends. Several of the facets, of which there are twenty-two in all, are saddle shaped and seem to have been developed by abrasion of the cobble while it was hung across a gap between two fixed cobbles or bowlders.

FIG. 4.—Detail view of end of cobble 2293. (See text.)

The general characteristics of chink-faceted pebbles may be summarized as follows: They are all of basalt, which is practically the only rock of the region, and vary from 3 or 4 centimeters in diameter up to cobbles of 20 to 30 centimeters. The most common general shape is subangular. A few are rather well rounded, whereas others are essentially angular fragments. The distinctive features are best stated in the form of an itemized list of characters.

1. May be composed of any available durable rock.
2. Sizes include entire pebble and cobble range.
3. General shape varies from angular to subspheroidal and is not necessarily distinctive of any particular previous process of shaping.
4. The facets are superimposed on the general shape of the pebble.
5. The facets are relatively numerous; as many as twenty on a single pebble may commonly be found.
6. The facets are of all sizes, from tiny ones on corners to larger ones covering a large part of one side of the pebble.

7. The facets are smoother than the remainder of the surface of the pebble.

8. The facets may occupy all possible situations on the surface of the pebble. Most commonly they are found on the more exposed parts of the pebble, but in some instances are strikingly developed on the deeper re-entrant parts of the surface.

9. The areal shape of the facets is likewise extremely variable, including subcircular, long and narrow, triangular, and irregular forms with straight-lined or curved margins.

10. The surface configuration of the facets includes concave, plane, and convex forms.

11. The facets have for the most part well-defined margins. Where they meet other facets or the old surface at a considerable angle, strikingly sharp, clean, and straight or moderately curved edges are developed. Only the larger facets which coincide closely with the old sides of the pebble and are poorly developed show indefinite margins.

12. A few facets show clean and regular grooves. In some cases these grooves are to be regarded as facets of special form superposed on the earlier facet.

13. The facets are not etched or affected by any sort of minute differential action.

The most distinctive characters are those enumerated under headings 5, 8, 9, 10, 11, and 12.

These pebbles are produced by the action of waves on rock fragments or pre-existing pebbles which have been imprisoned in interstitial positions between the larger bowlders of a very stable bowlder beach. When the major fabric of a beach is not disturbed by waves for periods of perhaps some tens of years, pebbles are found between the larger bowlders which are free to partake of some limited sort of motion, such as sliding, rocking, or twisting, but are definitely prevented from turning over and over. These pebbles are actuated by the force of the waves which wash in and around the network of bowlders and are caused to rub in a manner which, though not rigidly controlled, is very definitely constrained. In this way the various facets are developed, commonly not more than four or five being formed in any one position of constraint, but others being formed when a general shake-up in the beach enables the pebble to

assume a new position of constraint. The chink-faceted pebbles found by the writer were in place in the chinks in which they had been most recently abraded. At all localities, those in the lower part of the beach were being shuffled by the waves at the time of his visit, and some were taken out from under water.

The essential conditions required for the formation of such pebbles appear to be persistence of moderate wave action and stabil-

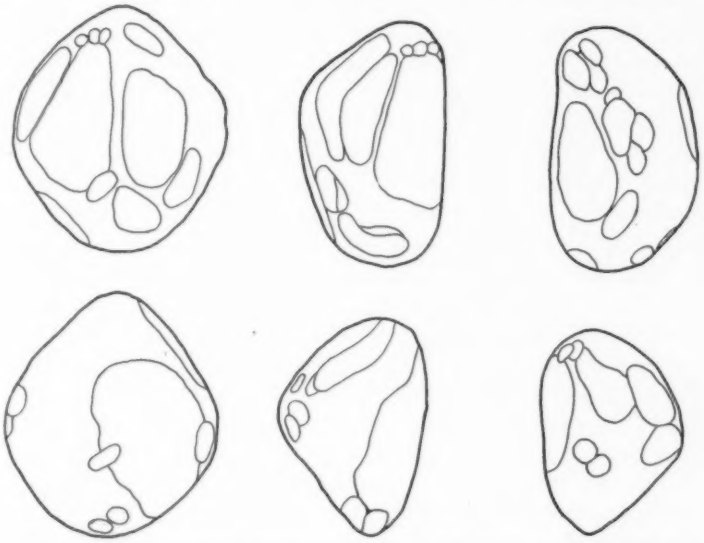

FIG. 5.—Diagrams showing pattern of facets on pebble 1420*A* from six different directions. Length of pebble 82 millimeters.

ity of the main fabric of the beach. The south-shore Molokai beach consisted of basalt bowlders and blocks ranging from 1 to 4 feet in diameter and resting on an old mass of conglomerate consisting of similar bowlders cemented in a matrix of calcareous sand. The Halawa beach was not observed to rest on a conglomerate, but some of the lower bowlders appeared to be more or less cemented together by the growth of various marine organisms.

Observations subsequently made at the various localities listed above made it more and more apparent that stability of the beach is a most important factor. At many of the Lanai localities the pro-

cess is more likely to appear at and near the beach end, where the bowlders are in part banked against the rock mass of the adjacent headland, and in the middle portion of such beaches. At most of the Lanai localities the process seems less distinctively and pronouncedly developed than at the type localities on Molokai. However, the apparently greater perfection of the process on Molokai is probably due to the writer's increased ability to recognize all stages of the process as he worked from the earlier to the later localities. Doubtless many places where the process only is moderately active were passed over before the writer's attention was attracted by the conspicuous features of the south-coast locality on Molokai. On most of the beaches where chink-faceted pebbles were found, the surfaces of the larger bowlders were grooved or scored or otherwise bore the marks of special local abrasion. On beaches composed of well-rounded cobbles and bowlders which bore the surface aspect of being subject to frequent general and violent rearrangement, repeated searches were made for chink-faceted pebbles, but none were found.

The positions of the pebbles in the chinks were as various as their faceted surface patterns would lead one to expect. Some lay between the sloping and slightly hollowed sides of two adjacent bowlders. In a few places they were freely removable from a deep chink from above, but in most instances escape even at the top was sealed by one or more bowlders, and the beach had to be disturbed in removing the pebbles. In two or three places, several chink pebbles were thrown together in one chink and took part in a complicated mutual constrained abrasion in addition to that wrought between them and the larger bowlders. In some of these places it was possible with much trial slowly to rearrange the pebbles one after another until one could be removed, thus freeing the rest, but the necessary combination of readjustments was apparently one extremely unlikely to be brought about by wave action. It seems probable that some of the pebbles occupying chinks which are open above are thrown up and overturned by strong waves and occupy different positions in rapid succession.

Chink-faceted pebbles differ from glacial pebbles in the large number of facets, the seeming fortuity of their distribution, and the lack of striae. They differ from sand-blasted pebbles in the lack of

etching or differential treatment of the surface and in the sharply controlled "subsequent" character of the facets.

While it is possible that conditions favoring this process may in rare instances be found in streams, it seems on analysis far less likely that they will be. The conditions on beaches which favor such action and the general opposite character of stream conditions are enumerated below.

1. A stable fabric of coarse material with a relatively small amount of fine material. Coarse stream-gravel deposits are more commonly covered or choked by finer detritus.

2. An intermittent to-and-fro movement of the water. Stream flow is in the same direction at all times and is relatively steady.

3. A dashing, swashing, upward movement of water into a previously unsaturated part of the beach structure. Stream flow is mostly downward and mostly into continuously saturated masses of gravel or other sediment.

4. Constancy of conditions at a given place over long periods of time. Stream regimen is subject to frequent and great fluctuations. Return annually or more frequently to a given set of conditions is conceivable but is in general unlikely.

From consideration of the points enumerated, it will appear that chink-faceted pebbles may practically be considered as exclusively of marine or lacustrine origin.

No measurements have yet been made of the rate at which the chink-faceting process goes on, but it is believed to be relatively rapid. From the unceasing character of the abrasive action during much of the year, and its strong localization, it seems probable that a distinctive chink-faceted pebble may be developed in a decade or two. After the development of good-sized facets, the process becomes much slower, and doubtless some of the pebbles are the result of much more protracted abrasion.

From the foregoing descriptions it is apparent that chink-faceted pebbles are quantitatively of little importance and that they make up but a trivial fraction of the whole mass of marine gravel formed on any coast. Nevertheless it seems likely that they are present in many ancient marine and perhaps lacustrine gravels, and that they will be recognized if careful search is made in favorable situations.

A NOTE ON THE ELASTICITY OF SOME MINERALS AND ITS MEASUREMENT

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ABSTRACT

The Gaston rebound tester is used to determine the relative elasticities of various minerals. Under this test fluorite, pyrite, quartz, and garnet are shown to be more elastic than steel. The remarkable rebound of 97 per cent was obtained on garnet, the elasticity of the ball itself being only 92 per cent on this scale.

The measurements on elasticity of minerals carried out by Tutton[1] and other investigators required complicated apparatus, but the results so obtained gave absolute values. In many lines of geologic investigation, however, figures representing relative elasticities are of considerable service. The following paper gives the results of the adaptation to mineralogy of an apparatus used in the testing of metals.

Metallurgical tests have usually been made to determine hardness rather than elasticity, and specially designed apparatus for this purpose are Turner's sclerometer, Brinell's testing machine, Keep's drill, and the scleroscope of Shore. With each of these, the specimens are given permanent deformations. When a measure of the elasticity is required, the stresses applied must fall below the elastic limits of the materials. This condition is fulfilled in the Gaston rebound tester (Fig. 1) described in detail below. The method consists in dropping a hardened steel ball from a standard height on to the specimen under examination and measuring the height of the rebound. The dimensions of the ball are such that in the case of metals there is no permanent deformation. The differences between this instrument and the scleroscope of Shore are:

[1] A. E. H. Tutton, *Crystallography and Practical Crystal Measurement* (London, 1911), pp. 911–23.

GASTON REBOUND TESTER

A steel ball, $\frac{3}{16}$ inch in diameter and weighing 7.2 grains, is used.

The fall is 8 inches (200 mm.).

Impact is 57-inch grains.

Rebound on hard steel is 92 per cent.

There is no friction on the glass tube and no piston action.

SHORE SCLEROSCOPE

A diamond-pointed steel drop-weight, weighing 36.4 grains, is used.

The fall is 10 inches.

Impact is 364-inch grains.

Rebound on hard steel is 70.5 per cent.

The drop-weight acts as a piston in the glass tube.

In the Gaston rebound tester here used, the testing element is a specially prepared steel ball of the dimensions given above. It is lifted by means of a magnetized needle to a height of 200 mm. and permitted to fall freely by gravity on to the horizontal surface of the test specimen. The height of drop is divided into a hundred divisions so that the scale gives the height of rebound directly in percentage of distance of fall. The motions of the ball take place within a glass tube, whose inner diameter is $\frac{3}{8}$ inch, attached to a column by means of an arm with two joints. The column itself is screwed into a solid base provided with three leveling screws. In the actual testing the ball must fall freely within the tube. To insure this, a level is fitted to the top of the tube and the latter is brought truly vertical by means of the leveling screws.

As in the case of the Shore scleroscope, attention must be paid to the mass of the specimen examined. If the specimen is small, a low reading will result. It was found, however, that there was no variation when the volume of the mineral examined was greater than about a cube of 2-inch side. The error arising in the case of smaller specimens is shown in the following example. A calcite crystal weighing 1 ounce gave a rebound of 70 per cent; another crystal weighing 14 ounces gave a rebound of 73.5 per cent.

The data listed was obtained by measurements made on crystal faces of minerals. Wherever possible, cracked specimens were avoided, but sometimes the only material obtainable was fractured to some extent. Tests on fractured and unfractured crystals of the same mineral showed that so long as care was taken to avoid cracked portions, the readings were practically the same, or if any error exists, the data is slightly low. For obvious reasons, no measurements were made on minerals showing signs of alteration.

Owing to irregularities on the surface of the mineral and the consequent oblique rebounds, the values obtained were not always exactly alike. The values given below are those which were consistently high and which, consequently, give a true figure for the mineral. In the actual testing at least one hundred readings were made for each reading recorded.

TABLE I

Mineral	Weight of Specimen in Ounces	Height of Rebound, Percentage Rebound
Garnet	14.5	97*
Quartz, prism face	5.5	95.5
Pyrite	20.0	95
Quartz, pyramid face	5.5	93.5†
Fluorite	64.0	93
Obsidian	1.5	93
Labradorite	14.0	90
Aragonite		74‡
Calcite	14.0	73.5
Hematite	25.0	72.5§
Selenite	10.0	32.5

* Slightly below 97 per cent, perhaps between 96.5 and 97 per cent.

† The support for the test on this face was poor, so that it is possible that the reading is somewhat low.

‡ The specimen used was small and the surface was not smooth. The reading is certainly low.

§ The support for this specimen was poor and the reading is low

For comparison, the readings obtained for different metals and alloys are given.

Nickel-chrome quenched steel	92
Bronze, special	60
Bronze, medium	40–45
Babbit metal	30

In the consideration of the foregoing results there are several points to be noted. In the case of bronze, for example, the modulus of elasticity is much below that of the ball used in the testing, consequently the deformation at impact is mostly in the specimen, and the rebound is due almost entirely to the elastic qualities of the bronze. In this case the figures obtained give a true measure of the elasticity of the metal. As the elasticity of the specimen approaches that of the ball, the elasticity of the latter comes more and more into the equation. It is obvious, then,

that if the material tested has a higher modulus than the ball, the readings will be low since the deformation will be more in the ball than in the specimen. The results given must therefore be considered in the light of this fact, and the values for garnet, quartz, and pyrite are relatively lower than they should be. The best

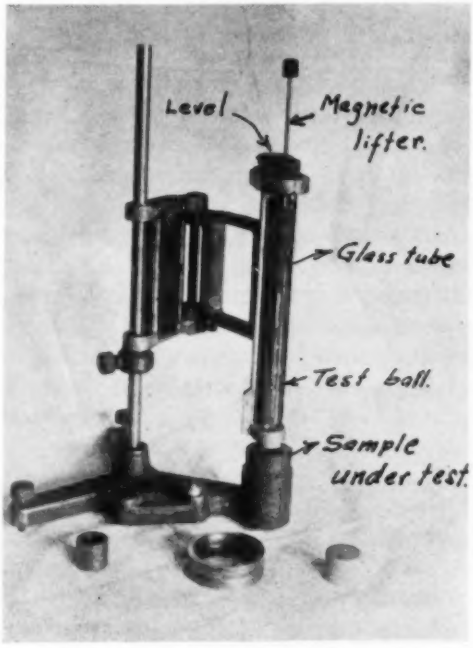

FIG. 1.—The Gaston rebound tester

method to carry out these tests would be to use a ball of the same material as that tested. The value for garnet, under such conditions, would be very high indeed, since the average of the steel ball (which itself has a value of but 92 per cent) and the garnet gave a rebound of 97 per cent.

In conclusion, the writers wish to express their indebtedness to Mr. Gaston for permission to use his instrument and for the photograph here reproduced.

ROCKY MOUNTAIN STRUCTURE

COMMENT

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The article[1] by Mr. Flint on this subject in a recent number of the *Journal of Geology* is a valuable summary of our knowledge of the salient features of one of the greatest mountain chains of the continent, presenting, as it does, an excellent résumé of the facts and an impartial outline of the theories of deformation, framed by various geologists to account for them. Being addressed to students, the discussion may, perhaps, advantageously be supplemented by presentation of certain suggestions regarding the mechanics of the structures, more particularly related to the phenomena of wedge-shaped mountain blocks and the development of overthrusts and underthrusts. In his final paragraph Flint states that the mechanics of the wedge-shaped ranges described by R. T. Chamberlin are as yet unknown. In a strict sense that is so and must always remain so, since we can never see the process in action, but there are mechanical principles by which we may approach an understanding that is consistent with the facts.

It is probably safe to assume that most competent geologists recognize the compressed condition of the zone of the Rocky Mountains and will accept the inference that the compression has affected an underbody of notable depth, i.e., a mass extending down into the earth to a distance of 100 kilometers, say. Whatever the depth, the underbody may be assumed to consist of rock masses which are continuous in the sense that there are no megascopic open spaces and the body is under a load which imposes upon it the condition of "an elastic, brittle mass, presenting great resistance to deformation" (Becker).

[1] R. F. Flint, "A Brief View of Rocky Mountain Structure, Studies for Students," *Jour. of Geol.*, Vol. XXXII (1924), pp. 410–32.

This being assumed, we may follow Becker, as quoted by Flint (p. 431), in concluding that rupture would take place along the lines of maximum shearing stresses. The development of shearing of this type can be seen in Plate XCIII, *Mechanics of Appalachian Structure*, and the final stages of that model are also given on page 277 of *Geologic Structures*. Similar structures showing overthrusts are to be seen in other models of that series. In referring to these models, however, the student should remember that the deformation of the upper parts of the models was controlled by the greater relative strength of the materials and by the artificial conditions of confinement. They are not to be interpreted as according, necessarily, with nature. The production of wedge-shaped blocks, such as Chamberlin postulates, and their vertical displacements are, nevertheless, clearly illustrated. The original models were 40 inches long. Assuming that that represented 40 miles, the corresponding vertical displacements obtained by compression amounted to 10,000 feet, more or less.

The models illustrate displacements along shearing planes produced by compression. According to observed facts, the Rocky Mountain zone has been strongly compressed. By deduction from studies of the effects of compression Chamberlin has reached the conclusion that the mountain masses are wedge shaped underneath. And that is the shape which would result from shearing under compression. The circle of observation and inference seems to be fairly complete. It may, however, be further tested by an appeal to mechanical principles and geologic history.

Whatever the origin of the force of compression, that force must have accumulated gradually. We must give it a geologic age or ages to gather to the point where it could overcome the resistance of the rocks to deformation. It had, therefore, the opportunity to penetrate the underbody of the continent, to disperse in the mass, to diverge from its original azimuth or upward or downward toward the zone of least resistance, to be reflected or resolved into components on impinging on any surface whatsoever, and to develop a counter-force or resistance equal to itself at any particular point. That that resistance was developed follows from the fact of compression.

Pressure and resistance are equal, and their mechanical effects will be the same as long as there is no movement. When movement does take place, it is the direction of least resistance which determines the direction of displacement. In the disregard of the latter law may be found the explanation of a great deal of fallacious reasoning regarding the source of the forces which have compressed the foundations of mountain ranges.

If we assume a horizontal, compressive stress pervading the Rocky Mountain zone, say from some pre-Laramie time on, we may reason from the orogenic activity of that age that the pressure had then risen to the point at which it was adequate to deform the underbody of the zone. Folding, in the proper mechanical sense of that term, could not develop in the rocks of the underbody, whereas shearing was the inevitable form of mechanical deformation. The underbody must therefore have been divided by shearing planes into rhomboidal prisms, which, under conditions of excessive pressure, would ride on each other as the mass shortened horizontally and grew in vertical dimension. The size of the original prisms was a function of the law of least work, as applied to the particular materials under the actual conditions, and the original dimensions are undeterminable. They may be assumed to have been greater than the present distinct mountain blocks, for the further development of dislocations must have subdivided them.

At the time when rupture was initiated along shearing planes, the relation of the shearing must have been identical with reference to the original force and the resistance, or counter-force. Those opposed forces being by assumption horizontal, the direction of least resistance would be upward and the effect would be to elevate a prism, producing at the surface a plateau or mountain ridge. This is the simplest form which the wedge-shaped range could take. In order, however, that the wedge might be elevated, the masses abutting against it on either side must be forced together, as may be seen in the models already referred to. They also must shorten horizontally, and in consequence must dispose of volume in one or more ways. Thinking of the reaction as progressing at a depth at which chemical changes may take place, we may postulate an increase in density or the alteration of granular rocks into schists

as methods of adjustment, the schistosity being oriented in the vertical plane. Mechanical adjustment, on the other hand, would be accomplished by shearing into more and more minute prisms and by their mutual riding over or past one another. The extreme condition of subordinate shearing and displacement is a form of flow, perhaps the principal mechanical form in solid rocks.

The superficial effect of shearing in the deeper masses appears at the sides of the upthrust wedge in outward overthrusts. Since action and reaction are equal, such thrusts may develop symmetrically on both sides of a wedge-bottomed range, but in general, since notable horizontal displacement characterizes them, the overthrusts will exhibit the greater horizontal shift away from the active source.

The downward extension of the plane of the overthrust would in such a case pass into the plane of the original shear, and the wedge-bottomed range would ride forward as part of the overthrust block. This means that flat-lying thrusts of this type curve downward to a dip of about 50° and pass into the fundamental planes of dislocation. In applying the idea to Rocky Mountain structure and to other great horizontal displacements we fail, however, to get a sufficient horizontal component of movement from the possible vertical component. This difficulty has led me to incline to the view that the mechanics of shear and of intrusion of molten masses may have co-operated in producing the horizontal shifts, the former having divided the masses into blocks which could be displaced and the intrusions having shoved them aside.[1]

It is clear that the wedge-bottomed range is *underthrust* from both sides, yet may exhibit at one or both sides a fault which we describe as an overthrust. In general, it would seem that we are right in describing an overthrust as an overthrust, for it is more than probable that the superficial fragment has moved over the relatively still lying mass beneath it, but the fact of the existence of underthrusts is undeniable and they may be important factors in the elevation of a ridge or range. The development of over-

[1] N. S. Shaler, "The Crenitic Hypothesis and Mountain Building," *Sci.*, II (1888), 280–81. Walter Penck, "Der Sudrand der Puña de Atacama." *Sächs. Akademie der Wissenschaften Abhandlungen der math. phys. Klasse*, Vol. XXXVII (1920), pp. 316–58.

thrust or underthrust is a purely mechanical accident, from which we should not draw too firm a conclusion in dealing with wedge-bottomed structures.[1] It is otherwise with Highland structure.

The Coast ranges of California exhibit examples of the development of faults by shearing, which are unsurpassed by any as yet described elsewhere. The San Andreas fault, 600 miles long, is such a shearing plane. In connection with the deformation which has taken place on that great rift and others parallel with it, the type of wedge-bottomed mountain block has been developed in all

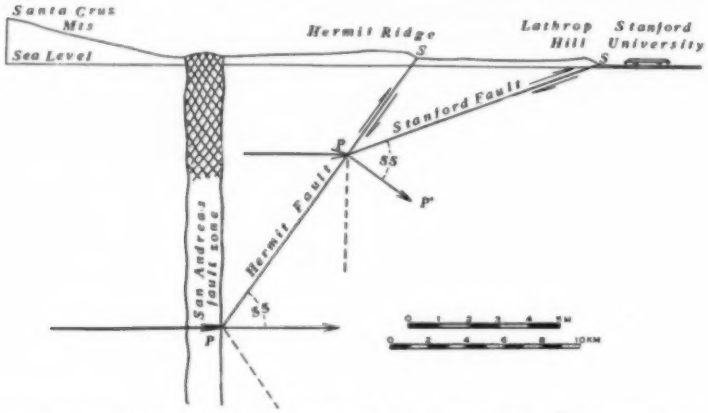

FIG. 1.—Diagram showing the relations of the San Andreas, Hermit, and Stanford faults.

sizes, from "horsts" involved in the fault itself to considerable ranges. The great shearing planes did not, however, emerge at the surface with the angle of dip which would characterize a plane of that origin under ideal mathematical conditions of equal resistance in all directions. There being an upward direction of least resistance within the range of their action, they curved upward toward it and assumed a nearly vertical attitude; that is, they became upthrusts.

The development of subsidiary faults took on various forms, but all of them apparently according to the laws of shear. Ap-

[1] C. W. Hayes and B. Willis, "Conditions of Appalachian Faulting," *Amer. Jour. Sci.* (1893), 3, 46, 257–68.

pended is an illustration drawn from the local facts at Stanford University. There are three faults—the San Andreas, Hermit, and Stanford. Assuming the first of these to be the original upthrust, the Hermit is interpreted as a shearing plane caused by pressure acting horizontally against its eastern wall. The Hermit having become a plane of separation, the pressure P, impinging upon it, would be resolved into its components and the one perpendicular to the Hermit fault would produce shears, of which the Stanford thrust is the expression.

The comparison of Rocky Mountain structure, Great Basin structure, and Coast Range structure offers a very fruitful field of research in which many types will appear. They must, however, whatever their character and relationships, all be explained according to the laws of mechanics as applied to the deformation of elastic bodies.

A NOTE ON THE MICROSCOPIC RELATIONS OF SULPHIDES AND SILICA IN BLAST-FURNACE AND CONVERTER LININGS

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ABSTRACT

A microscopic examination of the linings of a copper converter and of a lead blast furnace is described with a view to deducing criteria for the discrimination between the formation of sulphides by anhydrous melts and by hydrothermal agencies.

In view of the stress that has been laid on the possible formation of sulphide ore bodies by the injection of nearly anhydrous melts, it becomes of considerable importance to know if microscopically there is any means of distinguishing such deposits from those formed by hydrothermal processes. Stutzer[1] and Vogt[2] have dealt with the occurrence of sulphides in slags, but unfortunately a detailed description of the nature of the occurrence of the sulphides is not given. In order to obtain criteria, if possible, an examination was made by the writer of specimens of "corroded" linings from a lead blast furnace and from a copper converter. The former was obtained from Mr. A. B. Young through the kindness of Mr. Victor C. Heikes, who supplied also the latter material.

LEAD BLAST FURNACE LINING

The material came from near the top of the crucible lining from the smelter at Midvale, Utah. An examination of polished sections gave the following results:

The specimen is traversed by small veins, which run in all directions and are very numerous. Sometimes they are close so that they form a network isolating particles of silica. The boundaries of the veins in some cases show parallelism, but just as frequently there is no correspondence between sides. From veins there diverge smaller

[1] O. Stutzer, *Zeitschr. prakt. Geol.*, Vol. XVI (1908), pp. 119–22.

[2] J. H. L. Vogt, *Die Sulfidsilikatschmelzlösungen* (1918).

branches stretching into the silica masses. These latter veinlets do not appear to follow contacts between grains. Though the sides of some of the veins are roughly parallel, yet in detail the parallelism is not exact and the sulphide-silica contacts are very irregular. With the low power this irregularity is easily seen, and with the high power it is even more evident.

Within the veins there are frequently found relic fragments of silica. These show irregular boundaries, and here again the contact is ragged in detail. That these fragments are remnants is shown by the fact that their isolation can be observed in all stages of progress. What appears to be a network of veinlets when followed along sometimes becomes a single vein of the larger dimensions. Elsewhere a thin stringer of sulphide may fork from a vein and rejoin it farther on, thus isolating a part of the silica.

In the main, the position of the veins has been determined by the contacts between the silica grains, and sulphide areas are very irregular in form. When, as is frequently the case, the sulphides have worked their way into the silica from the main veins, a difference is noted, for there the sulphides show a decided tendency to develop a globular form. That the globular form is not the result of cavity filling, but is due to replacement, is shown by the ragged nature of the contact under high power. Figure 1 gives a *camera lucida* drawing of the occurrence of the veins.

Though the vein type of occurrence just described is the more common, another relation also exists between sulphides and silica. The sulphides may be present as apparently isolated globules of varying dimensions embedded in the silica. The isolation is more apparent than real. Detailed inspection shows that in the majority of cases minute veinlets connect these spherical masses with other sulphide bodies in the section. In the few cases where such connections are not observed, the assumption is justifiable that the connections are present in a dimension not cut by the plane of the section. With the low power the sulphide-silica contact appears rounded. With higher magnifications these contacts are seen to be ragged. The veinlets which connect with these spherical masses also show irregular outlines against the silica. In places, fragments of the latter mineral occur within the veinlets and are evidently relic particles.

Figure 2 gives a *camera lucida* drawing of the occurrence just described. These globular masses have gained their present position by replacement of the silica. It seems probable that the difference

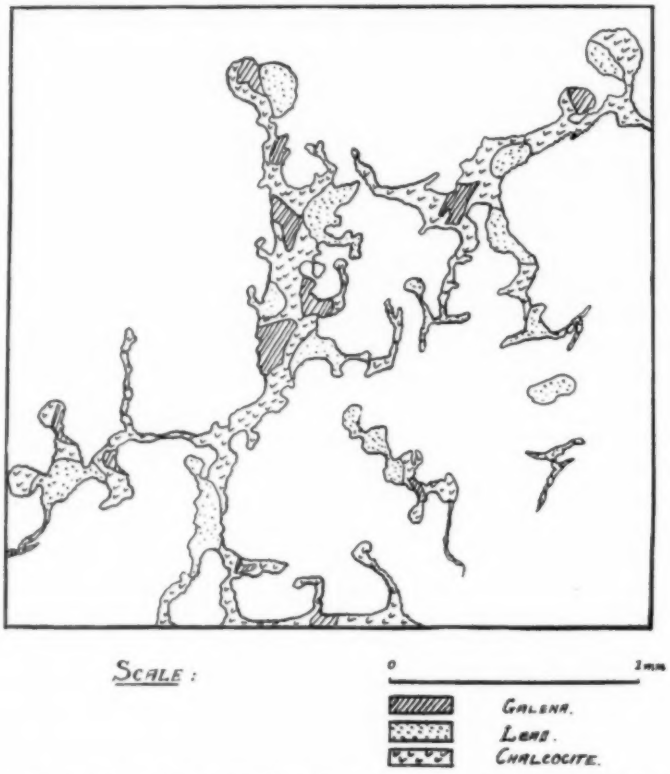

FIG. 1.—Camera lucida drawing under reflected light of veinlets of metallics in silica. Note the general similarity to ordinary hydrothermal replacement except for the tendency of the metallics to form rounded masses against the silica.

between them and the globular offshoots from the main veins described above is one of degree only.

In addition to polished specimens, thin sections of the material were also examined. These verify the observations under reflected

light. The general distribution of the opaque material has been determined by the grain contacts, and where offshoots of metallics occur, they frequently tend to develop a roughly globular form. There are also present apparently isolated spherical masses of opaque material. Figure 3 is a *camera lucida* drawing showing the relationships just described. The silica grains themselves are composed mainly of brownish glass, but this is also true of the fresh brick.

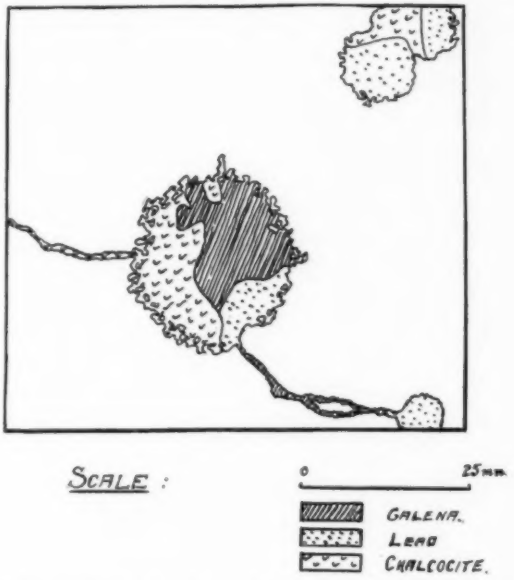

FIG. 2.—Camera lucida drawing under reflected light of two of the globular masses of metallics almost wholly inclosed in silica.

The components of the veins and spherical masses are chalcocite, galena, lead, and copper. No one of these replaces another.

From the study of these specimens the conclusions reached are these: The structure resembles that seen in ordinary hydrothermal replacements in that replacement has proceeded along the contacts of the rock units. Further, veinlike character is found here, as in ordinary replacements. The replacement in this case is not to be de-

scribed as a corrosion. A difference from the hydrothermal type lies in the tendency shown by the metallics to develop a globular form. This latter phenomenon finds no counterpart in hydrothermal replacements.

Since the silica has been replaced, one naturally inquires where that mineral has gone. So far as can be seen with the microscope,

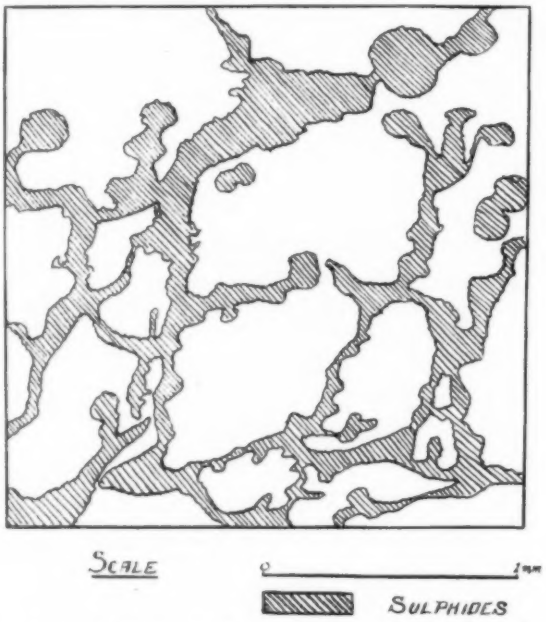

FIG. 3.—Camera lucida drawing in transmitted light of metallic veinlets in the silica.

the silica does not occur in the metallics. One is forced to the conclusion that the silica has passed out, probably as an iron silicate, through the small passages now filled with chalcocite, galena, etc. Vogt[1] has described the occurrence of spherical masses of sulphide in slags. He regards these as inclusions. The cases, however, are not similar, since the occurrences described in this paper deal with

[1] *Op. cit.*

a mass of silica which has never been fluid. It would correspond in the field to the action on the wall rock of a nearly anhydrous melt.

COPPER-CONVERTER LINING

The material examined was part of the siliceous bottom of a converter of the International Smelting Company, Tooele City, Utah. It is representative of the bottom of the furnace down to a depth of three or four feet.

Macroscopically it is seen that the boundaries of the matte and silica are rounded. Examination with reflected light under both low and high powers gives the same conclusion. Whatever irregularities occur are rounded in outline. The term "corrosion" is appropriate here.

In places the sulphides have penetrated the silica in small veins. The latter have evidently followed fissures in the silica, since the sides of the veins correspond. Isolation of fragments of silica occurs. Examination with the high power shows that, generally speaking, the contacts of sulphide and silica are rounded in detail. There are, however, many cases where for a short distance the contact is sharp. When this is the case, it is found that on the other side of the vein there is a corresponding sharp face, showing that the vein is a fissure filling. There are a few cases where the contacts could be described as ragged.

Examination of thin sections showed that the contours of the matte against the silica were rounded. The veins of sulphide occur in a very narrow zone around the contact and frequently have formed along the contacts of the silica grains, though they also occur cutting across the latter, filling cracks. The parallelism of the sides of these veins is not so well marked here, but the general relations are as seen in the polished sections. Between the silica and the matte proper there is a zone in which the silica has been so filled with grains of sulphide that only small portions of the former can now be seen. Figure 4 gives a *camera lucida* drawing of the relations of matte and silica as seen by transmitted light.

The matte itself consists of an intergrowth of a light-blue and a reddish-blue sulphide present in about equal amounts. The former answers to the microchemical tests for chalcocite, while the other

corresponds to none of the ordinary ore sulphides. Included within this intergrowth there are small bodies of other sulphides which also do not correspond to any of the ore sulphides. Nowhere in the sections examined did any mineral occur comparable to chalcopyrite.

For this particular case the following conclusions are reached: The dominant process has been corrosion. Veinlets occur, but these are in the main fissure fillings. The veinlets are confined to a very narrow zone around the sulphide. These features make the occurrence

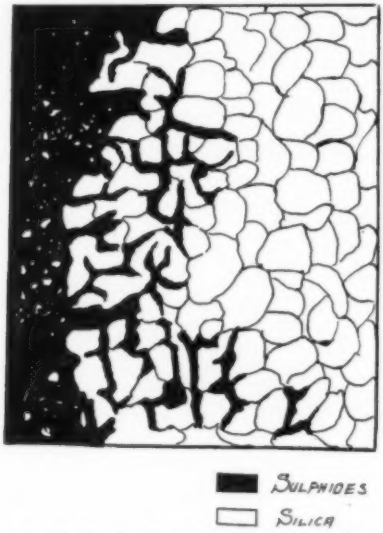

FIG. 4.—Camera lucida drawing in transmitted light of the contact zone between matte and silica showing the small veinlets of the former in the latter.

quite distinct from the hydrothermal type of replacement. Another difference seems to exist, namely, that though its necessary components are present, no chalcopyrite is found. It may be that the formation of that mineral is dependent on some agent or agents not present in such an anhydrous melt as is found in a copper converter.

CRITERIA DEVELOPED FROM THIS STUDY

Melts that presumably are nearly or quite anhydrous are capable of effecting replacement. The form of this replacement may

be veinlike or of a corrosive nature. In the former case, where the veins have eaten their way into the silica they tend to develop a rounded, bulbous outline. Further, the sulphides tend to form globular replacements within the silica, these globular masses being connected by small replacement veinlets to the larger sulphide masses.

The limitations of the present investigation must be stated. In the first place, the only mineral other than the metallics present was silica. The pressures existing at the time of the formation of the sulphides were low and the duration of the processes short. The specimens also are from material never more than at the most about one foot from the main mass of the melt.

In conclusion, the writer wishes to express his indebtedness to Professor Bastin for his advice and criticism.

MUD CRACKS FORMING OVER WATER

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INTRODUCTION

Geological literature contains many references to mud cracks or shrinkage cracks, but little seems to have been written concerning their forming as observed in nature. While engaged in collecting vertebrate fossils in the Bad Lands of South Dakota, the writer witnessed the development, under unusual conditions, of a type of mud crack.

OCCURRENCE OF THE CRACKS

The Bad Lands, as is commonly known, are cut here and there by creeks, dry except in time of rain, save where "water holes" may occur in the deeper spots. The floors of these creeks are normally strewn with sand and gravel, but about the water holes, through the accumulation of fine sediments in still water, the beds are covered with dried mud, abundantly cracked in typical polygonal fragments. Only the upper layer of perhaps a quarter of an inch in thickness shows these structures. Due to its thinness, the forming blocks commonly curl up.

The water of the water holes is covered with a thick, scumlike deposit of fine mud. Upon pushing this aside, much as one does the scum accumulating on top of a cup of cocoa, potable water is exposed beneath. The peculiar condition, however, lies in the fact that, while still plastic and underlaid by several inches of water, the scum begins to shrink and show outlines of polygonal fractures, at times even opening to expose narrow lanes of water. As the water beneath the scum gradually sinks into the ground or evaporates, the cracking scum settles and becomes stranded upon the creek bed. Further desiccation results in the production of the actual cracks along the already established lines. Final drying out curls up the layers.

Figure 1 illustrates the process as outlined. At the left of the center may be seen the scum with its developing cracks as it lies upon

the surface of the water in a water hole. Near the head of the pick the material is settling down upon the creek bed. To the right of the pick may be seen the fully developed cracks.

ORIGIN OF THE CRACKS

The cause of the phenomenon is not quite clear, though climatic conditions suggest an explanation. Intense sunshine is the rule in summer, with temperatures of over 100° F. common. Shade is lacking, and hot dry breezes blow much of the time. Therefore,

FIG. 1.—Mud cracks developing about badland water hole

evaporation from the surface of any water bodies tends to be rapid, and, but for the accumulation of the scum, the water holes would soon go dry. The scum appears to offer a fairly impervious insulator to retard evaporation from the underlying water. That some water does rise through the scum is attested by its moist condition, but this seems to be sufficiently overbalanced by evaporation from the upper surface to cause the scum to shrink. Shrinkage produces the fracture outlines. In advancing this explanation, it should be noted that, shortly after a rain, the scum, being of uniform surface, does not show the crack structures. The cracks then commence to develop as evaporation supplants precipitation.

REVIEWS

Block Diagrams and Other Graphic Methods Used in Geology and Geography. By ARMIN KOHL LOBECK. New York: John Wiley & Sons, Inc., 1924. Pp. 206, figs. 288.

This is a book of helpful suggestions for the teacher or field geologist who wishes to present pictorially the surface features of an area or to represent diagrammatically the underground structure. It contains an excellent elucidation of the principles of perspective and their application in constructing block diagrams of land forms, the use of graphic methods in solving geological problems, principles of the isometric type of perspective drawing, special methods for the preparation of more elaborate types of diagrams, field sketching, and suggestions for drawing crystals.

The striking feature of this work is its unusually abundant illustrations of land forms, which include most of the common physiographic types. Graphic methods, in fact, have been employed to such an extent that the book consists almost entirely of diagrams. It should prove very useful to teachers of geology.

L. F. A.

The Stratigraphy and Fauna of the Hackberry Stage of the Upper Devonian. By C. L. and M. A. FENTON. Contributions from the Museum of Geology, University of Michigan, Vol. I. New York: The Macmillan Co., 1924. Pp. 260, figs. 8, pls. 45.

The Hackberry represents the youngest Devonian known in the Mississippi Valley. The evidence at hand indicates that the Hackberry fauna is of northwestern rather than eastern derivation, and that attempts to correlate the Hackberry with other formations will be more productive if the Hackberry fauna rather than eastern faunas be taken as the basis for identification.

The contents of the publication are very well arranged and consist primarily of carefully prepared descriptions and illustrations of Hackberry fossils.

L. F. A.

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SUPPLEMENT

THE ANALYSIS OF GASES OBTAINED FROM VOLCANOES AND FROM ROCKS

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INTRODUCTION

In 1912 Day and Shepherd visited Kilauea for the purpose of collecting the gases emanating from that vent and determining the temperatures of the lava. The results of that expedition were embodied in their report published in the *Bulletin of the Geological Society of America*, Vol. XXIV (1913), p. 573. The essential facts noted were that the temperature was variable between 1,000° and 1,200° and that the gases consisted chiefly of water vapor. Since that time the writer has continued the study of such volcanic gases as have been available, and has begun the study of gases obtained by heating rocks *in vacuo*. In large measure the work thus far has necessarily been a development of methods rather than their application.

PART I

COLLECTION OF THE SAMPLE

It is obvious that the conditions under which a gas is collected are of critical importance. Gas liberated in the depths, usually at high temperature, as it approaches the surface passes through various rock formations, some igneous, some sedimentary, each of which is capable of adding to or subtracting from the initial composition, as well as of altering the proportion of the constituents by catalysis in cases where equilibrium has not been attained. This possible alteration is most apparent in gases collected from submarine eruptions. One cannot predict the reactions between the hot lava and the ooze of the ocean floor, nor can he fail to see that the gases have been admirably washed by bubbling through some fathoms of sea water. After so serious a chemical attack, the chemical composition of the gas which finally reached the surface would seem to bear little obvious relation to that of the gas originally given off by the magma. It has been less readily evident that similar alterations could be produced during the subterranean movement of gases or magmas containing them.

One cannot be sure that similar alterations have not been induced in the gases from fumaroles or even from volcanic vents. It is possible, of course, that with old and well-established vents the walls of the fissure have been coated by reaction products to such extent that some of the issuing gas may have come from the original source; some sort of equilibrium might be supposed to have established itself. Nevertheless, the gases from any vent are found to vary, not only with temperature and climatic changes, but also with the never ending readjustments under ground.

It is entirely credible that some fumaroles represent, not juvenile gases, but the distillation product of strata which have been reheated either by the intrusion of an igneous body or by a shifting of geotherms from any cause. It is probable that relatively small pressure changes affecting deep masses would result in a release of gases from the strata affected. In whatever way the release of gases is effected, they are always exposed to both gross chemical and catalytic alteration on their way to the surface. When we recall the almost insuper-

able difficulties introduced into the study of gas reactions by the surface effects of the containing vessels, the dominating importance of the "absorption tower" through which all these gases must pass becomes more apparent.

CLASSIFICATION OF VOLATILES

We may divide the volatiles roughly into three or four divisions: (1) volcano gases, that is, those issuing from the volcano vent during an eruption; (2) gases obtained by heating rocks and minerals *in vacuo* (closely related to [1]); (3) gases from fumaroles, which may be either "primary," that is, within the active crater, or "secondary," that is, located around the crater in older rock or in the lava streams; (4) gases from wells, caves, and mines; in general, the subterranean atmosphere. None of these classes is to be differentiated sharply from the others, and none is free from contamination by the others.

1. *Volcano gases.*—These gases are not necessarily uncontaminated magmatic gases. The fact that blocks of limestone are ejected at Vesuvius shows the probability of deep-seated contamination. Similarly, it is not surprising that in the gases which Dr. Jaggar collected with great care at Kilauea in 1919 some air was always found, however promising the source. Even the most superficial examination of the porous, shattered nature of the volcano edifice must arouse serious doubts as to the probability of securing uncontaminated gases.

There is always a strong temptation to accept too literally the textbook diagrams of magmas in basins below volcanic vents, and to think of them as simple liquids somewhat like geysers. To the writer it seems much more likely that we are dealing with masses which are not liquids at all from the standpoint of our daily experience. We may well hesitate to treat magmas, which are indeed liquids in the physico-chemical sense, as if they were limpid fluids possessing both the external and internal mobility of water solutions.

Nor is contamination by air our only difficulty. Whatever may have been the initial composition of the gases collected at Kilauea, they have reached the surface in a practically complete state of oxidation, exception being made of sulphur. Even the unusual sample

collected at Kilauea in 1912 by Day and Shepherd[1] should be regarded as an oxidized gas, although there was not sufficient nitrogen in this gas to justify the assumption that air as such was the chief oxidizing agent. At or near the surface, subterranean oxygen is probably more generally available than has been supposed. This follows from the fact that the surface lava is singularly porous. For example, it was at first hoped that by collecting the rapidly chilled glass, a sufficient quantity of the native gas would remain sealed in its vesicles to permit an analysis when the glass was crushed *in vacuo*. The hope proved illusory, and we found that after pumping the air out of the system, no amount of crushing (cold) liberated gas. The evidence indicates that these vesicles are intercommunicating and the mass minutely fractured. Again, the diffusion of a gas seems little altered by the fact that it is diffusing against a back pressure of some other gas, and from the shattered nature of the volcanic pile we may infer that from the time it begins its upward movement, the gas or the magma containing it is constantly reacting with the more highly oxidized country rock and subterranean atmosphere. The fact that the oxygen which diffuses in is removed from the system or "fixed" implies that a more or less continuous diffusion of oxygen toward the invading magma will take place. Nevertheless, we must perforce assume that the gases collected from a rising magma are as near magmatic as we may hope to obtain.

2. *Gases obtained from rocks and minerals.*—Gases obtained by heating fresh lavas *in vacuo* may be presumed to be residues of those originally in solution in the lava when it reached the surface. In the case of plutonic rocks or minerals such an assumption is less readily evident and will require much study.

3. *Fumarole gases.*—These vary in all degrees from the fumaroles alongside an active volcanic vent to the hot-air caves in regions where volcanism has long since ceased. The primary fumaroles might be expected to yield gases closely related to those collected from the lava itself. This is no doubt true, but our observation at Kilauea implies that such gases not only are contaminated by air

[1] E. S. Shepherd, *Bull. Hawaiian Volcano Observatory*, Vol. VII (1919), No. 7, Table II.

but are also gravely altered by irregular condensation. This is at once a disadvantage and an advantage, depending upon what one is seeking. It is a distinct disadvantage if one is studying the gases from the lava, because not only are the fumarole gases chiefly air and water, but the sulphur compounds are concentrated and unordered. Thus, at the Devil's Kitchen at Kilauea, as at other hot spots within the crater, SO_2, SO_3, and S_2 were being evolved, naturally in no definite ratio; while in the Sulphur Banks, where vegetation has an influence, occasional H_2S adds to the chemist's perplexity.

Somewhat farther removed from an active vent we may expect the gases to be contaminated, not only by reaction products resulting from the seepage of ground waters down into the heated region, but also by the general subterranean atmosphere and distillation products from the heated country rock. Obviously, between the magmatic gases and the gases of fumaroles the relation must eventually become exceedingly tenuous. On the other hand, fumaroles offer the distinct advantage that they concentrate the small quantities of both the magmatic and the rock distillates and allow the detection of elements which would otherwise escape notice, though the actual composition of the gases collected is more difficult of interpretation than that of the gas collected from the lava itself. These facts emphasize the importance of much more careful and exacting examination and analysis of the rocks through which both the first and third classes of gas must pass on their way to the surface. Such work is being done for the Katmai region, and there seems to be a large mass of data for the Italian group, though it has not yet been systematized as it should be.

4. *Gases from wells, mines, and springs.*—In general we may assume that there is a continuous slow diffusion outward of gases from the earth's interior, and to this we may apply the name subterranean atmosphere. At present we cannot pretend that the composition of such an atmosphere is known, and in any event it is so subject to local disturbances that we can do no more than infer its existence. The difficulties of analyzing such gases as may be collected, for the infinitesimal amounts of all but the ordinary constituents, make the task too great at present. Nevertheless, it is time

we collected such data as may be available, even if most such suffer seriously because of lack of geological data and the effect of the formations through which the gas reached the surface.

Gases in Rocks

If, as we suppose, the gases were in solution in the magma and are released by the reduced pressure when the lava reaches the surface, then it would seem a simple matter to reheat the rock *in vacuo* and determine the gases which remain in it after it has cooled down. This determination has been undertaken by several investigators and notably by Chamberlin.[1] Unfortunately, these investigators were chiefly concerned with proving that there were gases in rocks and apparently regarded the water as of no significance. A notable exception is A. Gautier, whose work both on the gases obtained from rocks *in vacuo* and on the possible reactions of water with rocks needs to be confirmed and extended. If, however, we grant the presence of hydrogen, carbon, and oxygen, then the water present is important, and the unfortunate fact that we cannot distinguish sharply between adsorbed water, water in solution in the rock, and water resulting from oxidation of the hydrogen of the magmatic gases is not a sufficient reason for ignoring the water altogether. In fact, we have now ample proof that water is the chief constituent of volcanic gases, and its determination is imperative. It is therefore doubly unfortunate that so much work should have been done determining only the relatively minor fixed gases and ignoring the one dominating constituent which in no small measure determines even the ratios of the fixed gases to one another. Equally unfortunate is the failure to determine the less volatile constituents, such as the halogens and sulphur, since, as we shall show later, fluorine sometimes exceeds carbon dioxide in the volume relations of these gases.

Even where some of the other constituents have been determined, it has been deemed sufficient by these pioneers to extract the gases from rocks with little or no regard for the composition of the rock and for its geological relationships. For pioneering work these omissions are natural, but it is obvious that before any notable

[1] R. T. Chamberlin, "The Gases in Rocks," *Carnegie Inst. Wash., Publ. 106*, 1908; A. Brun, *Recherches sur l' Exhalaison Volcanique*, Genève, 1911.

generalizations can be firmly grounded, much more detailed investigation will be necessary. It is entirely possible that when more systematic analytical work has been done, our petrologic views may require a considerable revision. In this work the minor constituents and volatiles, quite properly ignored in pioneer work, must receive the same consideration now given to the major constituents.

Although we do not yet know in what condition the gases exist in rocks, their presence may be regarded as amply proved. It might be supposed that the gases pumped from the chilled spatters of the Kilauea lava would bear a definite relation to the gases collected from the fluid lava except for the less volatile constituents, and in a broadly general way this is true for any given volcano. The less volatile constituents might be supposed to be concentrated in the lava, and would appear then among the gases obtained by heating the lava *in vacuo*. So long as the data are so scanty, no definite relationship can be read out of the figures. The less volatile compounds are of course present in greater amounts. It will be evident that no definite relationship has been shown for the gases taken from the molten lava itself at the Kilauea crater. Instead of a reasonable uniformity, the composition varies with each sample taken. This might have been predicted, since mere observation of the crater suffices to demonstrate that there is no fixed composition. Some fountains show the violet-brown fume of boiling sulphur, while others show none. Some orifices show blue flames, and others with good seeing show none. In other words, there is no reason to assume that any sort of equilibrium exists at this vent, in spite of the fact that the activity here is sustained over amazingly long periods.

That similar conditions exist at other volcanoes seems highly probable. Vesuvius passes through several gas phases during an eruption, and Mr. Perret finds that the beginning of a period of activity at all volcanoes he has studied is marked by the dominance of the halogens, while the cessation of such activity is indicated by the increasing dominance of sulphur compounds. At Kilauea the halogens are seldom present in amounts detectable by field tests, while sulphur is always present. It is doubtful whether hydrogen has often been present at Kilauea in quantities sufficient to furnish explosive eruptions, although explosive eruptions have occurred. On

the other hand, explosions which from their violence and "tone" are probably due to a fairly rich hydrogen mixture seem not uncommon at the Italian vents. Such explosions, however, seem not to be the major factors in what are called explosive eruptions, but rather unusual accumulations of explosive mixtures under special though unknown conditions.

In passing it may be noted that it is a reasonable supposition that the dominance of the halogens in the opening stages of an eruption is what might be expected from the reheating of the country rock by the rising heat. If so, then the final sulphurous stage may imply that these gases represent the composition of gases from the deeper strata; that is, more nearly the magmatic gases which after the clearing out of the vent are free to approach the surface. An equally valid explanation would be that the more volatile constituents are easily set free, and the less volatile, e.g., sulphur, are longer retained in the cooling lava. In any event, we are confronted by a very complex problem for which we have as yet no solution. It is our hope that by establishing a more critical point of view and more accurate methods this paper may serve to stimulate others to more detailed observations upon which the final solution depends.

METHODS OF COLLECTION

From the preceding it is evident that in collecting gases the observer's judgment as to what constitutes a good source of gas is of considerable importance. At Kilauea, for example, a red-hot vent showing a flickering blue flame is no guaranty that the gas is air free. A vent of this sort vitiated our vacuum-tube collection in 1912. On the other hand, the Dutch Oven (Fig. 1)—a completely inclosed spatter-cone situated over a large and persistent fountain, from which the first 1912 collection was pumped—yielded the most satisfactory gas which we have ever examined. It was unfortunate that we were not prepared to use vacuum tubes also at that source. On the other hand, the pump-and-train system which we used did serve to collect the minor constituents, so that some idea of the order of magnitude in which they were present could be formed. With vacuum tubes, even those of half-liter capacity, the minor constituents can seldom be determined.

FIG. 1.—The "Dutch Oven" at Kilauea, 1912

An ideal vent is, of course, one safely accessible, with a gas flow strong enough to maintain a steady flame outside the orifice. Sometimes such a vent can be improvised by partially blocking a vent otherwise too open, but for the most part finding a suitable source is a matter of luck. The operator then does the best he can, assured that his best will be none too satisfactory.

The most systematic collection of gases ever made was that of Dr. T. A. Jaggar, director of the Hawaiian Volcano Observatory, in 1919. A comparison of the analyses with the field notes is most instructive as to the difficulties encountered in satisfactory collection.[1]

Vacuum Tubes

The usual vacuum tube has the tip drawn out to a fine point so that the point breaks on contact with the walls of the opening and allows the tube to fill. Obviously such a tube possesses serious limitations. If, as is usually the case, the gas to be collected is at a higher temperature than the surrounding air, it is practically impossible to seal off the tip without removing it from the source, and the temperature change fills the tube with air before it can be sealed off. For some fumaroles this can be improved by using a tip long enough to permit sealing off near the tube without withdrawing the tip from the fumarole. This convenience is rendered futile with moist gases, for the condensation in the long tip is lost or at least seriously altered and a quantitative determination becomes doubtful. If the gas is at a temperature above the softening-point of the glass, the tip usually melts down and refuses to break.

It might be supposed that if instead of a pointed tip the end of the collecting-tube were blown to a thin bulb, this bulb could be broken or would melt through. Another form has the collecting-end or tip thickened in such manner that under ordinary conditions it would surely crack off on reheating. These methods fail when the tube is introduced into the furnace-like vents with which we have worked, and further more, while the tip declined to crack when introduced into the source of gas, it was very apt to do so while being transported to the vent.

[1] E. S. Shepherd, "Kilauea Gases," *Bull. Hawaiian Volcano Observatory*, Vol. IX (1921), pp. 83–88.

We were finally forced to use a tube of special construction such as is shown in Figure 2. The tube volume may be anything desired, but we prefer one of 300 to 500 cubic centimeters. This volume can be obtained without making the tube too bulky for transportation. The collecting-tip *B* is the essential feature of the tube. This consists of about 40 millimeters of 12-millimeter tubing of moderately thick wall. In the rounded end at *D* is fused a thin plate of very soft glass. Glass such as is used for sealing in platinum wires will serve. This disk of soft glass is supposed to melt through before the thick walls of *B* have reached their softening-temperature. The larger size of *B* allows the incurving film of soft glass to pull through before *B* softens.

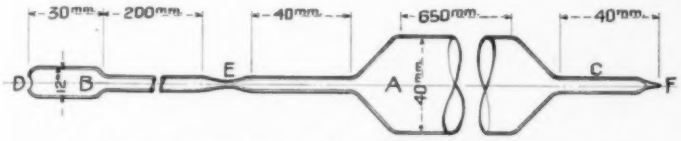


FIG. 2.—Evacuated tube for collecting volcano gases

It is advantageous if in making up the tubes the glass is slightly thickened and constricted at *E*. This makes it easier to seal off the neck of the bulb in the never too steady gasoline torch necessarily used in the open air and often in the wind and rain. About 4 centimeters of the small tubing are left at either end of the bulb for convenience in handling in the laboratory. Before sealing off at *E* one warms the lead-in tube between *B* and *E* to drive any condensed water and sublimate over into *A*. Copper wire for tying and asbestos paper shielding the tubes are at times advantageous.

It was this type of bulb which was used by us in the 1917 collection at Kilauea, as well as by Dr. Jaggar in making the 1919 collection. Our procedure in 1917 was as follows: The vacuum tube was wired to a long bamboo rod. The collector stood at the edge of the lake (see Fig. 3); during the intervals when the lake is rising this is safe enough, though a sinking of the lake surface is a signal for retreat. As the folded crust floated by, the tip of the tube was thrust as deeply as possible into the small openings from which small, hissing flames were rising. The bulb was held in this opening, much

as one plays a fish, until it was believed that the soft glass had pulled through and the tube filled with gas. Sometimes this filling can be noted by a sudden clouding of the tube. In any case, the tip is retained in the hot orifice until the glass has softened sufficiently to permit sealing it off by touching it against the hot lava and thereby sealing the tube. Under the most favorable conditions one is thus able to secure an excellent sample. Not infrequently the tube will

FIG. 3.—Method of collecting gases in soft-nosed tubes. Kilauea, 1917

crack in pulling off, and then the tip must be covered with a soft-rubber tube until it can be sealed at the torch. In this latter case, air is of course mixed with the gas. Nevertheless, this method is the most reliable we have found.

For cooler vents, these soft-nosed tubes are of no value, and the tube with a drawn-out tip must be used. This can be opened by breaking the tip against a rock, if there happens to be one in the vent, or by some mechanical device such as that used by Allen and Zies, who have described these methods elsewhere.

PART II

ANALYSIS OF GASES AND OTHER VOLATILE PRODUCTS

ESSENTIALS OF THE METHOD

No matter how great pains may be taken in collecting to avoid contamination by air, the collected gases will be found to vary from 0 to 100 per cent air. The persistence with which air can find its way into a vacuum tube which is apparently well placed in a glowing vent from which quite unbreathable gas is issuing is one of the exasperations of this work. If that were all, it might be dismissed with a suitable benediction, but the fact that such incredible contaminations occur is of considerable significance in throwing light upon the high degree of oxidation commonly found, and upon the permeability of the volcanic edifice.

It follows, therefore, that any scheme of analysis for these gases must take into consideration the possible presence of a large percentage of air and yet be sufficiently precise to give reliable determinations of the ten or a dozen constituents of the volcano gas under investigation. This requirement automatically excludes the usual methods of gas analysis, so that special methods—some of them none too good, it is true—and special apparatus are unavoidable. Bunsen's methods in Bunsen's hands were probably satisfactory, but the state of the literature indicates that he has had few successors. Hempel's methods are admirable for the purposes for which they were designed, that is, where the supply of gas is ample and not too much air contaminates the sample. Unfortunately, neither of these requirements can be met when dealing with volcano gases or the gases pumped from rocks *in vacuo*. No system employing liquid reagents can be satisfactory where, as in our case, the amount of some constituent may be but a few cubic millimeters or less. It is all too probable that many if not most of the analyses hitherto published are of limited application because of the fact that the analyst failed to appreciate the limitations of his analytical procedure and so mistook simple solubility for absorption. Added to this limitation is the fact that both pyrogallol and the copper solutions used for CO give off gas except under the most favorable conditions, and those conditions are precisely the ones which involve a maximum non-selective solu-

bility. This is the most probable explanation of the CH_4 reported almost unanimously, and it may be significant that the CH_4 reported is usually small and inversely proportional to the total amount of gas used in the analysis. Except for fumaroles, and of course mud volcanoes, there is no reason to expect any large quantity of CH_4, and our material has never given a conclusive test for it.

Since liquid reagents cannot be used in these analyses, we are compelled to use a mercury pump for moving the gas in the apparatus. It is not feasible to push gases around, even through capillary tubes, by means of mercury. The gas will cling to the walls with little regard for the law of gravitation, and allow the mercury to pass by. This is notably true of SO_2, and CO_2 is almost as contrary. Much exasperating experience has convinced us that however repugnant the complexity of the apparatus we propose, it is the only way whereby reasonably satisfactory results can be obtained. We have tried several promising simplifications, but have been compelled somewhat unwillingly to return to the system here described. Of course, for special purposes the apparatus can be simplified, with much saving of time. Several such pieces of apparatus have been described in the literature, some of them possibly without much experience of actual use.

If one has a very simple gas mixture and the quantities are fairly uniform, there are several clever devices available. One such is described by Ryder.[1] Similar apparatus was in use in the laboratory of the General Electric Company in 1912. Unfortunately, one cannot always choose his gas mixture nor be sure that the pressures will remain within the limits of the U tubes which sometimes serve so admirably in place of stopcocks. Nor has everyone a supply of liquid air constantly available. Guye[2] has described an apparatus for gases in metals. It will not serve for other than very simple gas mixtures.

Since we are compelled to pump the gas about from tube to tube, the solid reagents must act with reasonable speed, must not show too pronounced adsorptive qualities which would greatly retard the analysis, and they must not have an appreciable vapor pressure.

[1] *Jour. Amer. Chem. Soc.*, Vol. XL (1918), p. 1656.

[2] *Compt. rend.*, Vol. CLIX (1914), p. 154. *Chem. Abstr.*, Vol. VIII (1914), p. 3386.

This last means that they must not show a vapor pressure of 0.001 millimeters at the temperatures at which they are to be used. Catalysts seem to offer the most promising field for future improvement in methods, but for the most part they are too adsorptive, and those which contain manganese are to be avoided.

Summarizing our conceptions of a proper apparatus for this work, we may say that it has the following essential characters. The apparatus must be able to hold indefinitely a vacuum of 0.001 millimeters. It must be so constructed that once the gas sample has been introduced into it, there is no chance of losing the gas through faulty manipulation. The analysis may go wrong through carelessness, but the gas must not have opportunity to escape from the apparatus. The reagents must be specific and not adsorb the other gases. The reading-device must be sensitive enough to handle the small quantities of gas with which we are dealing, even in the presence of large amounts of diluting gas such as air. Not only must the vacuum hold as between the apparatus and the outer air, but it must hold as between the different parts of the apparatus. It must be possible to pass an inert gas through any adsorption tube and upon returning it to the volume bulb the reading must not have changed more than the limits of error of the reading-device.

Our present apparatus was originally based upon one described by Pamfil.[1] Unfortunately, his apparatus as described is satisfactory neither in its operation nor in its chemistry. The pump there described was intended to be automatic in action. This kind of mercury pump is possible, but in our experience it is not worth while. It may work well for a time, but at some inconvenient time the mechanism fails unpredictably and the analysis or the apparatus suffers. We therefore dispensed with the automatic feature of Pamfil's apparatus and retained only the control by means of an auxilairy mechanical pump and the atmospheric pressure. Rubber connections are inadmissible in a system of this kind, and Pamfil's use of a rubber stopper to join the absorption system to the silica tube in the furnace would be bad practice. Because there is always the serious danger of gas leakage through or along rubber tubing, and even more serious danger of fouling the mercury, it is unwise to use rubber con-

[1] *Bull. de la Section Scient. de l'Acad. Roumaine*, Vol. III (1914), p. 72.

nections to leveling-bulbs if the same mercury is to pass into the volume bulb. Fused-glass joints are desirable at all junctions, and where this cannot be done, as at the junction between the glass apparatus and the silica tube, great care must be exercised in making the joint if distillation products are to be avoided.

It is unwise to have stopcocks near the volume bulb or, in fact, near any bulb if both gas and mercury are to pass through it. Where unavoidable, the stopcock should be lightly greased and should be located as far away from the bulb as possible. The increased distance appreciably retards the time when cleaning the bulb will be necessary. Where feasible, the gas should be pumped through the stopcock rather than pushed through it by mercury, since the unavoidable grease will always hold up small amounts of gas. Moisture greatly hastens the fouling of mercury by stopcock grease. The flange joints which Pamfil adopted from Guye are a distinct help at those places where the absorption tube must be removed from the system and weighed; at all other places, it is wiser to seal the tubes direct and cut out the part when it has to be renewed.

Gases to Be Expected

From volcanoes or rocks the following gases are to be expected: H_2O, CO_2, CO, CH_4, etc., H_2, N_2, A etc., NH_3(?), S_2, SO_2, SO_3, COS, H_2S, Cl_2, F_2, HF, H_2SiF_6, SiF_4. This list is worth a few moments' reflection from the chemist's point of view. It will be noted that there are few of these gases which are not attacked by any reagent which might be applied to remove some particular one. In the case of several of them, even under the most favorable conditions, no precise method exists for their determination in the presence of one another, although, in common with most substances, a very precise determination is possible if only the gas can be separated out pure. It follows, therefore, that we can scarcely hope for more than approximations. In a general way one can foresee that H_2O, the halogens, and sulphur and its oxides must be determined gravimetrically. The remainder pass, along with some SO_2, into the apparatus for gasometric determination. The details for individual constituents will be discussed in the appropriate place.

It is worth while to make use of a condensing-tube just outside

the furnace, or the connection to the vacuum tube, cooled with carbon dioxide snow and chloroform mixture, to condense most of the heavier gases and vapors. Where large quantities of water are to be caught, such a system has value. In our experience, the carbon dioxide–chloroform mixture will hold up water very well, and neither that nor liquid air can be relied upon to catch water vapor which is moving rapidly through narrow tubes. Particles of ice form but continue on through the tube and out at the other side.

For those most uninviting rocks, the oily shales, some such condensing tube will have to be used, but that will be a research in itself, and a most unattractive one.

Sublimates

The sublimates from rocks are best studied separately from the gases. The separation, of course, is merely for convenience, since with these very small amounts special methods must be employed, and the purpose is to collect as large an amount of sublimate as possible. The collection of this sublimate may or may not combine successfully with the mechanical necessities provided for the collection and analysis of the more volatile constituents. In our still quite limited experience, we have seldom had enough sublimate to warrant more than a qualitative test. The chief sublimate is amorphous silica, which separates out in the cold part of the silica tube as a ring just at the point where the tube emerges from the furnace. In part, this silica deposit is due to the escaping fluorine. In part, it is probably due to silicon hydride. This gas seems to have other properties besides those mentioned in the literature, for there it is stated that the gas decomposes at 200°. We have observed its presence, or at least that of some easily decomposed silicon-bearing gas, whenever silica or a silicate is heated in the presence of hydrogen to about 1,100° or higher. We have inferred that the reaction is reversible in the sense $SiO_2+4H_2 \rightleftharpoons SiH_4+2H_2O$, but in any event, in the presence of hydrogen and at about 1,100° silicon is transported in some form which deposits metallic silicon on platinum and alloys it. We have mentioned this reaction[1] without, however, making any study of it. It would seem to be of sufficient geological significance to warrant further study.

[1] *Amer. Jour. Sci.* Vol. XXVIII (1909), p. 300.

Seldom have we found the halides condensed as such in the colder parts of the furnace tube, possibly because the halogens as set free combine with the hydrogen or water present in reactions which give the corresponding acids, and so pass on into the absorbing system.

Fluorine is apparently evolved in all three combinations when rocks are heated *in vacuo*, the major portion evidently as HF. At the higher temperatures the amount of SiF_4 increases. It is therefore important to pump continuously during a run in order to avoid any condensation of water, and consequent formation of H_2SiF_6 in the chilled part of the silica tube. If, as has happened with some of the former studies in this field where water was not determined, the gas from the furnace passes directly into a P_2O_5 bulb, some SiF_4 probably passed through the pump and was mistaken for CO_2 or perhaps Cl_2. It will be remembered that H_2SiF_6 is quite volatile at reduced pressures.

In our limited tests, the Kilauea lava is the only one which so far has given any notable sublimate, and that was a heavy sublimate of copper sulphide.

If the literature did not indicate the contrary to be the case, one would suppose it unnecessary to point out that in any study of sublimates a most rigid checking of the reagents used is of prime importance. This obvious faith in reagents casts serious doubt upon the "traces" of various elements which have been from time to time reported by a number of investigators. On the other hand, it may be true that traces of many and quite unexpected elements are to be anticipated, once a search is made for them.

ANALYTICAL PROCEDURES: GRAVIMETRIC METHODS

The analysis of the products, either those obtained from volcanoes or those pumped from rocks *in vacuo*, is necessarily divided into two divisions, the gravimetric and the gasometric.

Acid Gases

Whatever the original source of the gas, the gravimetric procedure implies first the absorption of the acid gases in $CaCO_3$ and Na_2CO_3. This takes place before the absorption of the water because many of these reactions will not occur readily with anhydrous reagents.

The Na_2CO_3 used was a specially pure sodium carbonate which had been analyzed and found relatively free from interfering impurities. None the less, a blank analysis was always carried along with the determinations on this material. The carbonate was dehydrated by heating in an atmosphere of CO_2 at 500°. The absorption bulb was a U tube of good quality with well-ground stoppers, of the valve type, and equipped with the connecting flanges described farther on. About 5 grams of carbonate are placed in the tube, and after standing in the balance case the tube is weighed. The carbonate is of course roughly weighed also. After the gases have been pumped over into the analyzing-apparatus, the bulb is removed from the train, cleaned, allowed to stand in the balance case, and weighed again. After this weighing, the tube is subjected to analysis by the scheme to be described farther on.

Water

After the removal of the more acid gases by the Na_2CO_3, the water is to be taken up by a P_2O_5 tube. There is here some difference of procedure, depending on the amount of water to be determined. Up to about 1 gram of water, it is feasible to absorb it in the tube here described. If the water amounts to much more than a gram, it is necessary to freeze it out with a mixture of CO_2 snow and chloroform. For a temperature of about −80°, chloroform is just as efficient as ether or any of the other solvents recommended, and is safer and more satisfactory to work with. When the other gases have been removed as far as possible, the tube can be separated from the apparatus and the water weighed and analyzed.

According to Travers, P_2O_5 is often contaminated by phosphorus, and he gives a method for treating the heated oxide in a stream of oxygen in order to purify it. We have not had this trouble and so have not tested the method. It is, however, important that the P_2O_5 be not brought in contact with organic matter. The tube or bulb must be thoroughly cleaned with strong, hot cleaning mixture, rinsed with distilled water, and dried by passing clean air through it. The use of alcohol and ether for drying tubes and bulbs is a source of many odd results. Practically never has such drying failed to introduce more impurities than we were striving to eliminate. Stopcock

grease must be prevented from working down over the glass wool or into contact with the oxide. Complete separation of the two is of course impossible, but the contamination can be confined to the relatively small passage through the stopper of the tube. We have had one shipment of glass wool which for some reason was greasy, and so as a general precaution we have been accustomed to pack the glass wool into a glass tube, start a current of oxygen through it, and heat up the tube. If organic matter comes in contact with P_2O_5, gases will be slowly given off which simulate a small leak, and such may cause endless trouble. The subsequent handling of the glass wool must be done with forceps or very clean and dry fingers. If the usual type of U tube is used, choking up may sometimes be prevented by running a twisted platinum wire around the U. Two small platinum wires twisted together and inserted before the oxide is added will start the gas currents going right and furnish a support for the phosphoric acid to cling to, thus keeping the tube open.

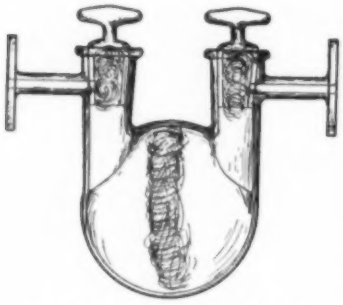


FIG. 4.—Phosphorus pentoxide tube

In order to get a maximum of P_2O_5 in a weighable bulb, we have adopted the form shown in Figure 4. Its advantage lies in its high absorption capacity without danger of choking up. The clean and dry tube has a partition of glass wool built up in it as indicated in the sketch. This is easily done with the aid of a wire or small glass rod. We find it advantageous to plug the stoppers also with glass wool. P_2O_5 is introduced by means of a small funnel and worked into the glass wool without, however, packing it down. Then the stopcock grease is lightly applied to the stoppers and any excess which may work out removed with a swab moistened with chloroform.

The obvious criticism of this form of bulb, that a long column offers a greater surface exposure for absorption, is of less moment here, since at these reduced pressures absorptions are much more rapid and efficient. We find it desirable to work some P_2O_5 into the

stoppers. This is done by a slight puff of air, which draws the powder up into the glass wool. Then a slight suction will draw enough moist air through to make the glass wool rather sticky. The object of this is to trap any powder which may subsequently tend to be drawn out of the tube should there be a sudden puff of gas through it.

After standing for a suitable time in the balance case, the bulb is weighed and connected into the train. When the operation is over, it is removed from the train, the flanges cleaned with chloroform and alcohol, the bulb wiped in the usual manner, allowed to stand, and again weighed.

We have had no evidence that P_2O_5 affects or is affected by any of the other gases with which we have dealt. Ammonia would of course be stopped by it, but we have not met with this gas in rocks as yet. The heavy hydrocarbons would be attacked, but these also have not appeared in our work.

Before taking up the analysis of the sodium-carbonate tube, it will be well to describe our methods of handling vacuum tubes, as well as the arrangement used where gases are to be pumped from rocks. This deviation from orderly procedure rests upon the fact that the analytic manipulations are so intertwined with the mechanical that they are best described together.

Handling of Vacuum Tubes

In this work one proceeds according to the necessities of the case rather than according to preconceived ideals of sound analytic practice. For precise determination either of the halogens or of the sulphur compounds, separate determinations under carefully controlled conditions are necessary. No such control of the conditions is possible where the material cannot be separated into different portions, and where the supply of material is scanty.

If, as should always be done, water and sulphur dioxide are to be determined, then mercury may not be used to displace the gas in a vacuum tube. Both of these vapors cling tenaciously to the glass, and the combination of course attacks mercury. Even dry SO_2 attacks mercury slowly, apparently a little more rapidly in bright light than in the dark, so that on standing for a day a distinct film will appear. In any case, it is necessary to drive the last of these

vapors from the walls of the tube by flaming it. It need not be heated very hot, but it must be flamed until it is too hot to be handled with comfort. Unless this is done, a notable amount of gas will be left in the tube.

This necessitates an arrangement such that the tube shall be accessible from all sides. Rubber connections being undesirable, we developed a special apparatus for opening the tube into the line

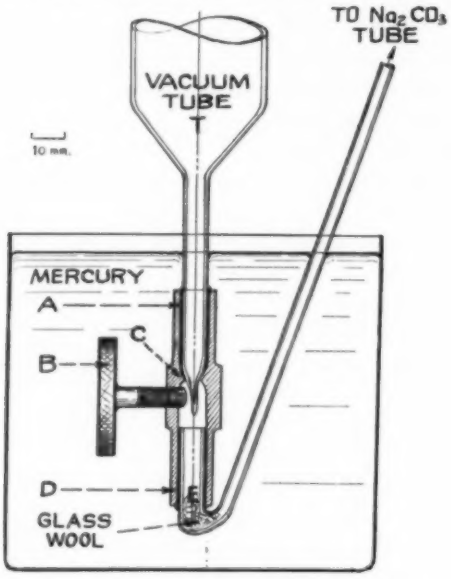


FIG. 5.—Apparatus for opening sample-tubes

of the analytical apparatus. The crushing apparatus (Fig. 5) consists of a cylinder *AD* which is turned out of a steel block, leaving a thicker wall about midway. In boring the cylinder a constriction is left at *C*, while through the thicker portion a screw *B* is set. This arrangement allows the pointed tip of the tube to come to rest opposite this screw *B*. The lower end of the cylinder has cemented in it the glass tube *E*, which is usually filled with a small, loose ball of glass wool. From *E* the exit tube leads to the Na_2CO_3 absorption tube or whatever the next stage of the apparatus may be. This

exit tube is preferably of 4-millimeter tubing, so that it is quite flexible and can easily be led around to attach to the next stage. Tube *E* is cemented in with De Khotinsky cement, care being taken not to get a ring of it at the end of *E*, and of course to use as little and expose as little as is consistent with a thoroughly tight joint.

The procedure is simple. The tip of the vacuum tube is first warmed to drive any water and sulphur out into the main body of the tube. The tip is given a fine scratch to insure ease of breaking. Screw *B* is greased lightly with heavy stopcock grease. Both cylinder *A* and the tube are warmed and given a light coat of cement. Then the tube is pushed down into *A* until the tip rests nicely on the ring *C*, and a good joint finished off in the usual manner. The tube is placed in its support, which allows the tip and crusher to dip under mercury in the trough. If everything else is in order, the whole system can now be pumped down as far as the tip and to the usual 0.001 millimeters. After being allowed to stand until it is certain that the system is tight, the cock on the Na_2CO_3 absorption tube is turned off and screw *B* is turned in until the tip of the vacuum tube breaks off. The shattered tip, along with perhaps some sulphur, etc., is caught by the glass wool in *E*. By slowly opening the cock on the Na_2CO_3 tube, the gas can now be allowed to pass slowly into the analyzing apparatus and the system finally pumped down again to 0.001 millimeters. In this last pumping it is necessary to flame the vacuum tube *T* with a not too bright flame, so that any gas or vapor clinging to the walls may be driven off, but not hot enough to volatilize the sulphur.

If a large amount of water, or water with sulphuric or other acid, is anticipated, the crusher can of course be turned upside down and protected by an improvised mercury seal. This arrangement permits driving over most of the water in the flaming process, though, as can be seen, it is a rather delicate and by no means attractive method. However, one does ultimately get the gases pumped over into the apparatus and sealed off at the far side of the P_2O_5 tube. While this sealing off may not be absolutely necessary, the two stopcocks of bulb 7 (Fig. 11) being closed between the intake tube and the apparatus, it is none the less a wise precaution to seal off the intake line and so to avoid the always possible leakage.

Analysis of the tube residue.—The vacuum tube is now removed from the crusher by gentle heating of the part *A* (Fig. 5). After inserting a small cotton plug into the broken tip to prevent chips of cement from getting into the tube, the cement is removed by gentle warming, scraping, and finally wiping with a rag moistened with alcohol. The tip is cut off near the bulb and placed in a 400-cubic centimeter beaker along with the glass wool and chips from *E* of the crusher. The tube is now rinsed with distilled water and the washings collected in the beaker containing the tip. After warming gently, this liquid is filtered through a paper filter which has been well washed with distilled water. The filter paper, cotton from the crusher, and the glass tip are set aside for the sulphur determination.

The filtrate may contain sulphuric acid, ammonia salts if any—they are seldom present—and the salts of the halogens. If ammonia is to be determined, the filtrate is made up to a known volume, divided into three portions, and the ammonia determined colorimetrically in one of these portions. A second portion is made slightly acid with hydrochloric acid (a measured quantity, of course, because a blank determination must always be made) and a little filtered barium-chloride solution added to the previously heated filtrate. This should precipitate any sulphate present, and after standing twenty-four hours any precipitate, however small, is collected on a carefully washed paper, ignited, and weighed. The sulphate gives the free sulphuric acid present. The third portion is made acid with nitric acid (acetic acid if fluorine is to be determined in the filtrate) and silver nitrate added for the determination of chlorides, in the usual manner. We prefer to collect this precipitate in a vitreosil Gooch crucible, taking the precaution always first to pass 100 or more cubic centimeters of distilled water through the filter and then repass this in order to collect any possible loosened asbestos fibers. The amounts often being small, this precaution is a wise one.

Fluorine

There is no satisfactory method for determining fluorine. Several methods suitable for special cases have been devised, but a method which can be generally applied has not yet appeared. There are two essential difficulties in the way of a satisfactory determination of this

singularly elusive element. The first difficulty is in separating the fluorine from the material under test. Obviously, if calcium fluoride is fused with an excess of silica, the fluorine should be driven off. Experience teaches that while most of the element will be evolved under these conditions, the last portions are very tardy about doing so. To make the work more interesting, fluorine tends to combine in unusual ways and lie down anywhere in the apparatus, so that while one may feel reasonably confident that what he has weighed is fluorine, he will never feel certain that the figure represents all of the fluorine which was present.

The second difficulty lies in the high solubility of the fluorides of the alkalies and alkaline earths. Treadwell determined the solubility of precipitated CaF_2 to be about 1 milligram in 100 cubic centimeters of water. This figure is for practical purposes apt to be conservative. If one collects the fluoride in a Munroe crucible, he will be able to observe that even smaller amounts of wash water will decrease the weight by a milligram or more. When we recall the ease with which the element forms silicofluorides and the high solubility of even its most insoluble precipitates, we are prepared to expect fluorine to show up at almost any point in an analysis.

Small amounts of calcium fluoride are carried down by the barium sulphate precipitate, and any change of weight on treating this precipitate with sulphuric acid and re-igniting may properly be accredited to fluorine, in our procedure at least.

In the vacuum-tube residues, fluorine is best determined in the portion used for the chlorine determination. The excess of silver is removed by means of sodium chloride, and the filtrate made alkaline with sodium-carbonate solution and brought to near boiling. An excess of calcium chloride is added, and the solution is then boiled a few minutes. The mixture of carbonate and fluoride is filtered through a Munroe crucible, using a minimum of wash water. It is not necessary to scrub the platinum dish or beaker at this stage. The precipitate is then washed out of the crucible and back into the dish, using a fine stream of water from the wash bottle. The crucible is placed in a small beaker or dish and half-filled with water to which a few drops of 10 per cent acetic acid are added. It is then set aside while the main portion of the precipitate is treated. Small amounts

of dilute acetic acid are added to the precipitate in the dish until the carbonate is almost completely dissolved. When this is judged to be about all in solution, the dish is placed on the water bath and evaporated to dryness. The dish is kept covered with a watch glass during the solution of the carbonate. After a short period of standing dry on the bath, the dish is removed and the calcium acetate dissolved by adding a small amount of warm water, a few drops of acetic acid (to make certain that all carbonate is in solution) and about an equal volume of filtered alcohol added, and the dish allowed to stand for a time. The calcium fluoride is now filtered off, using the Munroe crucible, and the precipitate washed with about 50 per cent alcohol to which a few drops of acetic acid have been added. Calcium fluoride clings tenaciously to the dish and must be brought onto the filter by the judicious use of a rubber policeman. If necessary, the last traces may be removed from the dish by wiping with a small piece of filter paper, which is dried separately and ignited in the crucible cap. After washing, the crucible is dried in an air bath at 110° and then ignited in the electric furnace at incipient red heat (600°). In the absence of an electric furnace, the crucible should be ignited briefly in the oxidizing flame. Any reducing-gases cause a loss of fluorine. After weighing, the precipitate is treated with a few drops of concentrated sulphuric acid, which is allowed to run down the sides of the crucible from a stirring-rod. The crucible is covered and the acid fumed off in a radiator of the type described by Hillebrand. The crucible is then ignited and weighed. The change in weight gives the datum for calculating the fluorine. A second treatment with sulphuric acid may be necessary if the amount of fluorine is large.

The method is not what one would wish, but is the only one available at present. With most vacuum-tube collections, the quantity of fluorine found will be very small, and the colorimetric method might be followed after the fluoride has once been separated from the other material.

Insoluble Residues of the Tube

We may expect here fluorine, and sometimes, though seldom, chlorine, and sulphur. The filter paper with the broken tip and glass wool

is placed in a 400-cubic centimeter beaker. A little distilled water is run into the vacuum tube, and a measured quantity of sodium-hydroxide solution added. Ten to 25 cubic centimeters is enough, and usually the sodium-hydroxide solution is made up fresh and used in several such analyses, thus saving unnecessary blank determinations. The tube is warmed and the alkaline solution run around in such manner as to dissolve any sulphur which may be in the tube. The solution is then washed into the beaker containing the broken tip. To the beaker is added a measured quantity of 2 to 10 cubic centimeters of hydrogen peroxide (we prefer a smaller quantity of Perhydrol, of which our present supply shows no sulphate and no chlorine test). The beaker is now brought to boiling and held there for a few minutes to oxidize the sulpide to sulphate. The solution is then divided into two portions, and the rest of the procedure is the same as that described for the water-soluble portion.

We must again insist that since the amounts are small, measured quantities of all reagents must be used and a blank determination carried along with the analysis. It will be found that a very careful check of the reagents is necessary, and one slowly accumulates a set of such reagents which he reserves for this kind of work.

As indicated above, fluorine must be expected to appear anywhere. Some indication of its amount will be supplied by the etching of the vacuum tube, though this is not specific, and of course after warming the tube with concentrated sodium hydroxide it will be more or less etched anyway. If, however, we are not dealing with a sulphuric residue in the tube and the amount of sublimed sulphur is not great, one can notice the etching, if any, when the tube is pumped dry.

If sulphur is not to be determined, then we may look for fluorine as follows: The vacuum tube is extracted with sodium hydroxide as for sulphur, the alkaline solution made acid with a known amount of sulphuric acid, filtered, a standard titanium solution added, and fluorine determined colorimetrically. Even then there is a chance that a great deal of fluorine will remain attached to the walls of the glass tube. Obviously this could be broken up and the fluorine determined by Hempel's method, but we have not tried this.

Where it is at all possible, we advise that a special search be

made for fluorine in the field. In the case of volcano or fumarole gases, a suitable absorption train will enable one to determine fluorine much more satisfactorily by absorbing it from a relatively large quantity of gas and then determining it in the absorbent. (See Allen and Zies on Katmai fumaroles, referred to elsewhere.) Because of this very unsatisfactory state of the methods for determining fluorine, we have not usually determined it in vacuum tubes, although we are well aware of its importance.

Procedure for Gases Obtained from Rocks

The situation is distinctly better when we undertake to analyze the gases obtained by heating rocks *in vacuo*. In this case we are able to absorb the fluorine before it has had an opportunity to lose

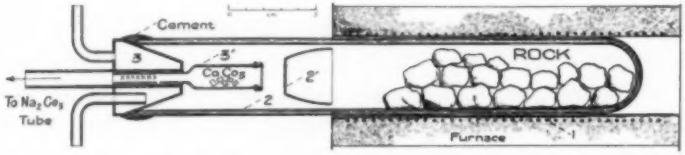


FIG. 6.—Apparatus for the removal of gases from rocks, and for the absorption of fluorine.

itself in too many other reagents. This development followed the observation that a cleavage fragment of calcite placed near the exit from the furnace tube became coated over with a skin of fluorite, as shown by chemical and microscopic check. We have therefore followed the arrangement shown in Figure 6. *1* is the furnace described farther along. *2* is the silica tube in which the rock is heated. *3* is the water-cooled plug used to close the silica tube and connect it with the rest of the apparatus. It will be described in detail later. *2'* is the platinum reflector used to protect the plug from the radiated heat from the furnace. *3'* is a silica-glass absorbing-tube. The constricted end fits into the exit tube of the plug, loosely, but tightly enough to hold it in position. This constricted portion is packed with crinkled platinum-foil wads between which a small wad of absorbent cotton may be placed to prevent any calcium carbonate's being blown out of the tube. The body of *3'* may be of any convenient size, say 1 centimeter, and is filled with pure calcium carbonate. This carbon-

ate must of course be analyzed for halogens and sulphur, other impurities being less important. It works just as well and is more satisfactory to compress the carbonate into pellets with a pill machine, using the least pressure which will make them hold together. The mouth of tube *3′* is closed with a piece of thin platinum foil which has been punctured by being placed on a sheet of glass and stabbed with a sharp needle. The object is to provide a diaphragm which allows a free passage of gas but with holes too fine to allow the carbonate to be blown about in case of an unexpected rush of gas. Under our conditions, this tube never gets warm enough for the calcium carbonate to show a measurable pressure of carbon dioxide.

At the close of a run, the plug *3* is detached from the silica tube, and tube *3′* removed. The platinum foil is carefully cleared of any carbonate dust, this being washed into a small beaker or, preferably, smooth platinum dish. The carbonate from tube *3′* is also washed into the same dish, and warmed gently. The calcium chloride is now filtered off, using a Munroe crucible, and chlorine determined in the filtrate. The separation of the fluoride is done as detailed above. The insoluble residue may contain CaF_2, SiO_2, and $CaSO_4$. It is collected in a Munroe crucible and gently ignited. Owing to the high solubility of calcium fluoride, the washing must be as little as one's conscience will permit, using very small additions of 50 per cent alcohol at a time. The silica might possibly be obtained by washing the precipitate in the crucible with hydrofluoric acid and again igniting and weighing. We have not tested the method. Usually the SiO_2 is minimal, the SiF_4 passing undecomposed through the *dry* $CaCO_3$, and a special study is needed to determine how to separate SiO_2 from CaF_2. After deducting the fluoride and silica, the remainder represents calcium sulphate and is computed as S_2. Few rocks will evolve SO_3 when heated *in vacuo*, so that sulphur may be treated as S_2. From the figures obtained for SO_3, F_2, and Cl_2 one obtains the data necessary to correct the total CO_2 for the amount set free from the calcium carbonate.

There are numerous criticisms to be made of this method. With rocks rich in sulphur, some sulphur may be expected to sublime and settle in the carbonate tube, and in the case of oily rocks one may expect the heavy hydrocarbons to make much trouble. Obviously,

in such cases special procedure will be necessary. SiF_4, if set free in the furnace and not decomposed by the water vapor, will pass the calcium-carbonate tube, at least in part, and will have to be sought in the sodium-carbonate tube. If, as we find advantageous, a freezing-bulb is used between the furnace and the Na_2CO_3 tube, any SiF_4 which escapes will decompose there and the fluorine be recovered. It might be supposed that the SiF_4 generated could be passed over into the gasometric part of the apparatus and determined there. This is entirely possible, but not if the other gases are to be determined. Rocks rich in chlorine or sulphate and low in water might give trouble, but we have not as yet had enough experience to suggest what variation of procedure may be necessary.

The Sulphur Gases

It is unfortunate that no entirely satisfactory separation and determination of the sulphur group is available under our conditions, any more than under the usual conditions of laboratory practice. With plenty of material, more or less satisfactory separation and determination of H_2S and SO_2 is possible in the absence of other disturbing factors. Nevertheless, one infers from the literature that the separations are by no means simple nor the results sharp, unless a very accurate control of the conditions is possible.

Fortunately for us, H_2S is not to be anticipated in volcano gases nor from normal rocks heated *in vacuo*, since at the temperatures involved it is supposed to be unstable. On the other hand, carbon oxysulfide (COS) is probably a common transient phase around volcanic vents. Since it breaks down readily into CO and sulphur, its separate identification is rather a matter for the field, and probably it is not seriously involved in the high-temperature reactions we have to consider. In fumarole gases its presence is to be expected.

Sulphur dioxide.—Under ordinary controlled conditions the determination of SO_2 presents many difficulties, and at reduced pressures these difficulties are not minimized. Any reagent which will attack SO_2 will also attack some of the other constituents of the gases with which we have to do. Such being the case, we have to select the best available method or not determine the SO_2 at all. It should be noted that at low pressures SO_2 is not absorbed appreciably by Na_2CO_3.

Where the supply of gas is ample, say 50 or 100 cubic centimeters, one portion of the gas is passed through the analyzing apparatus, the SO_2 being absorbed along with the CO_2 in the KOH bulb. This figure is then corrected by the value for SO_2 obtained in the other portion which is analyzed for SO_2.

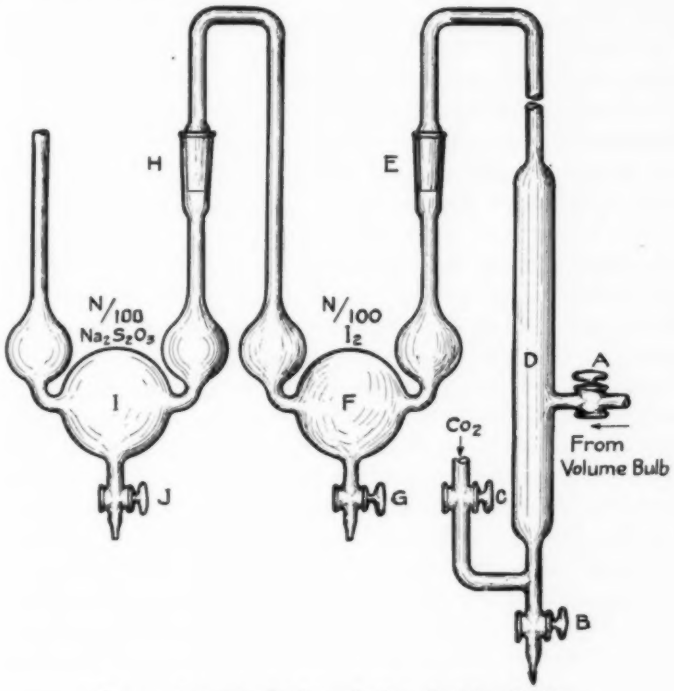


FIG. 7.—Apparatus for determination of sulphur dioxide

This is best done by passing a known quantity of the gas through N/100 iodine and titrating back with thiosulphate. In our apparatus as set up (Fig. 7), a special tube is led off from the outlet tube as *F* in Figure 11. This leads to a mercury trap *D*, one arm of which connects to the outlet tube from the volume bulb and the other to a generator *C* for pure CO_2. From *D* the gas passes through the ground-glass joint *E* to any suitable absorption bulb *F* containing N/100 iodine solution. This in turn connects by the ground-glass

joint *H* to a similar bulb *I* containing a known amount of the N/100 thiosulfate. In this way any iodine vapor carried over from *F* is trapped and accounted for when the thiosulfate in *I* is titrated. Suitable stopcocks to assist in manipulation are indicated at *A*, *B*, *C*, *G*, and *J*. *B* allows draining off the mercury, while *G* and *J* allow washing the standard solutions out of the absorption bulbs. Cock *A* is closed at all other times, and the tube between it and the volume-bulb outlet kept full of mercury. In practice, the thiosulfate is washed into the beaker in which the titration is to be made and then the iodine bulb washed into it. The back titration is then carried through at once. The absorption bulbs for SO_2 determination may be of any preferred type. We use a double-route spiral bulb made to order by a glass-blower.

As a matter of procedure, the air is first displaced in the absorption system by pure CO_2 before the gas is run in from the volume bulb. After passing the gas into *D* the CO_2 is again started and continued passing slowly for fifteen minutes, in order to wash over all the SO_2 into the iodine. This prolonged washing is not good practice, but is the only way to insure that the SO_2 which clings tenaciously to the glass tubing shall have passed into the iodine solution. By keeping the apparatus up to the ground joint *E* as dry as possible, the time required for getting all of the SO_2 over can be shortened. This procedure as sketched above gives satisfying results. Unfortunately, it is not applicable to the common cases where only a few cubic centimeters total gas are available.

In these cases we are forced to make use of the far from perfect lead-peroxide absorption. We have not found the commercial article satisfactory. Aside from impurities, the material has a high adsorption which greatly slows down the analysis. In other words, even where the peroxide is compressed into pellets, the adsorbed gases come off very slowly when one tries to pump them back into the volume bulb. Moistening the peroxide pellets with phosphoric acid to reduce adsorption leads to a slow evolution of gas, probably oxygen. We were therefore moved to use, instead of the precipitated peroxide, a roll of thin platinum foil upon which a thin layer of peroxide had been deposited electrolytically. This works much better and will serve to indicate the approximate amount of SO_2. However, some

attack on the hydrogen and carbon monoxide will occur, and so it is necessary to divide the gas to be analyzed into two portions, one of which passes through the peroxide tube, while the other has the CO_2 and SO_2 absorbed together. From this last the hydrogen and carbon-monoxide determinations will give the necessary correction for that portion which was used in determining the SO_2 by peroxide. This is all obviously unsatisfactory, but no other method has occurred to us.

Unsatisfactory as lead peroxide may be, it is the only available material we have found thus far. Next to it comes silver oxide, which, however, is irregular in action at 90°, below which temperature it does not react and above which the vapor pressure of the oxygen becomes appreciable. It also attacks hydrogen and carbon monoxide fairly rapidly.

The natural suggestion of manganese dioxide for this purpose is futile because all of the manganese oxides which we have tried have shown the volatility noticed by Travers. We have not tried to determine in what form the manganese distils over, but it will pass through 5 feet or more of tubing, as well as the P_2O_5 bulbs, and settle down as an iridescent film at the contact between the mercury and the glass of the pump. It even passes over into the volume bulb, ultimately rendering necessary a cleaning of the whole system. Since most of the catalysts suggested for separating carbon monoxide depend primarily on manganese salts, they are excluded from consideration in a low-pressure system.

Iodine pentoxide, which works well enough at ordinary pressures, is valueless for our purposes. We have tried out many absorbents for SO_2 and will mention a few merely to save others the disappointment of trying them. Alkaloids suggest themselves as possibilities, but the two tried, quinine and hydrastine, were not able to hold the SO_2, though they took it up readily enough. The quinine had the added peculiarity that after attack by SO_2 at these pressures it set free some hydrocarbon vapor, especially if there was oxygen in the SO_2. Since SO_2 must be removed before oxygen can be determined, the reagent was useless. Camphor and rubber absorb SO_2 greedily, but even on freezing fail to hold it. The alkali iodides are known to combine with SO_2 at low temperatures, and we investigated this series.

Unfortunately, they show several millimeters SO_2 pressure even at $-70°$, and so were discarded. In this series we examined the iodides of lithium, sodium, potassium, rubidium, caesium, silver, calcium, strontium, barium, and ammonium. None is of value, though potassium iodide gave the lowest vapor pressure. Ag_2CO_3 and $Ag_2Cr_2O_7$ are without effect at permissible temperatures.

It should be evident that the separation of both the halogens and the sulphur compounds is in a very unsatisfactory state. In its way, however, it is no worse than our knowledge of the form in which these elements occur. Until the analytical methods have been perfected and the gas reactions are better understood, we cannot hope to know much about the condition of these elements in the rocks. It is entirely possible that the results would mean just as much or more if computed back to the elementary condition, but a larger body of data must be available before any inferences will be justified. This line of thought is stimulated not only by the fact that in pumping gas from heated rocks in vacuo the actual ratios as between hydrogen, carbon, and oxygen compounds depend not only upon the temperature and rate of pumping, but also upon whatever the catalytic effect of the surfaces involved may be. Similarly, vacuum tubes such as those from fumaroles, or from Kilauea, which contain a great deal of water, free sulphur, and sulphur dioxide and trioxide, sometimes with hydrogen sulphide for good measure along with air, permit almost any degree of interaction of the constituents between the time of collection and the time of analysis. We have already shown that even from the best of gas collections at Kilauea there is no uniformity in the composition, so that perhaps we need be little worried about the actual composition, save perhaps the elementary. In the meantime, we must admit that the methods of analysis are far from precise and probably will remain so for some time to come.

GASOMETRIC METHODS

After the separation of the acid gases, the analysis of which has just been described, the gas passes into the volumetric apparatus for the determination of the so-called fixed gases. This group, however, includes the not easily fixable SO_2, some of which remained behind in the sodium-carbonate tube, but most of which will be

found in the volumetric section, where it should be promptly determined, since it slowly attacks mercury even when dry, and fairly rapidly if moist. In any event, the gas taken over is to be measured and if necessary the excess passed into the storage bulb. In this process it will be noted that one must pass all of the gas into the storage chamber, mix it thoroughly, and then draw back a portion for analysis, since the gas as drawn over varies appreciably in composition as between the first and last portions. Whatever disposition is made of the gas, there remain to be determined possibly oxygen, sulphur dioxide, carbon dioxide, carbon monoxide, hydrogen, hydrocarbons, nitrogen, and argon with the rare gases.

Sulphur Dioxide

SO_2 is to be handled as already described. Where the amount of gas is extremely limited, it may be necessary to omit this determination and take the total SO_2 and CO_2, since for most purposes the hydrogen and carbon monoxide are perhaps the more desirable values to have correct.

Carbon Dioxide

This is determined by absorption with solid KOH. There are no special details about this reagent except that it must not be the "purified-by-alcohol" variety. This sort gives off hydrocarbon vapors, and the fact will be noted that the bulb will not pump down and stay down. Such KOH may well be the origin of the hydrocarbons reported by some investigators. There may be some advantage in mixing a little soda lime with the KOH, though we do not know why. It seems to give rather cleaner absorptions. Working with KOH, one soon discovers that it is a very good dehydrating agent, and no special P_2O_5 bulb need be used in connection with this absorption bulb. Any water vapor which might escape is, however, taken care of by the numerous P_2O_5 bulbs in the system.

If SO_2 is absent, it is immaterial whether one removes the CO_2 or the oxygen first, but of course if sulphur dioxide is present, then that must be removed before the gas passes into the phosphorus bulb. Our preference is for removing the carbon dioxide first, the more so since this usually reduces the total volume of gas appreciably and so speeds up the always wearisome oxygen removal.

Oxygen

Obviously, oxygen has no place in a mixture of combustible gases issuing from a vent at 1,000° or more. And this is true whether we are dealing with molten lava or pumping the gases from rocks *in vacuo*. Pamfil noted with surprise that in his analyses he found oxygen a common constituent of the gases evolved *in vacuo*. However, Pamfil's analytical method arouses serious doubts. His method of determining oxygen was to pass the mixture of gases over red-hot copper. Since this meant passing hydrogen, carbon monoxide, carbon dioxide, sulphur dioxide, and possibly methane over red-hot copper, it is not surprising that he found a change of volume, but it would be unwise to regard that as evidence of the presence of free oxygen. There may be conditions under which free oxygen can be evolved as a transient phase, but we have discovered none. We have uniformly interpreted oxygen really present as due to air either in the supposedly evacuated tube or, more commonly, mixing with the gas after collection and before sealing off. In fact, it is only under the most favorable conditions that air can be eliminated. There is also to be considered leakage into the apparatus, the avoidance of which requires continuous checking up on the condition of the system. Consequently we make it a regular practice to subtract from any gas composition, as analyzed, oxygen with the normal equivalent of nitrogen, carbon dioxide, and argon, before computing the composition of the gas under analysis.

The use of liquid reagents being prohibited in a low-pressure system for minimal quantities of gas, it follows that the never very safe pyrogallol cannot be used for determining oxygen. Since heating the mixed gases must be avoided, one is finally forced to adopt yellow phosphorus as the reagent. Since, however, dry phosphorus does not react with oxygen, some compromise is necessary. There is the added difficulty that the vapor pressure of yellow phosphorus is appreciable (several hundredths of a millimeter) even at −70°, so some provision has to be made to remove the phosphorus vapor before it gets over into the mercury of the pumping system.

The final absorption bulb arrived at is shown in Figure 8. The preparation of such a bulb presents no difficulty. The phosphorus is contained in bulb *P*. As usual, the phosphorus is cast in small sticks

about 2 millimeters in diameter and these are cut into about 5-millimeter lengths, working under water as is customary. The upper end of the intake tube *E* is left a few centimeters longer than will be needed. The bulb is filled with water and the small phosphorus sticks introduced through *E* until the tube is filled loosely with phosphorus. The water level in the bulb is then lowered so that after wiping out the inside of *E* with a cotton swab, the tube *E* can be drawn down. Now the water is drained out of the bulb *P*, leaving only what clings to the walls and the phosphorus. This may amount to .5 cubic centimeter, and in any case is too small in amount to settle down into the rounded bottom of *P* and by freezing shatter the bulb. *E* is then sealed to the intake tube from the apparatus through stopcock *B*, and the outlet tube *D* may be sealed to its stopcock *A* at the same time.

From stopcock *A* (Fig. 8) the gas now passes through a tube of HgO. This may be of any convenient size, say 15 millimeters external diameter, and of course has the ends plugged with glass wool. Since the mercuric oxide is heavy and packs down rather tightly, we found that better results would be obtained by passing a twisted string up through the mass; the string is merely wound around a copper wire and placed in position before the tube is filled with the oxide. This permits the passage of the gas even when the pressure has been reduced to a few thousandths of a millimeter.

This mercuric-oxide tube stops the phos-

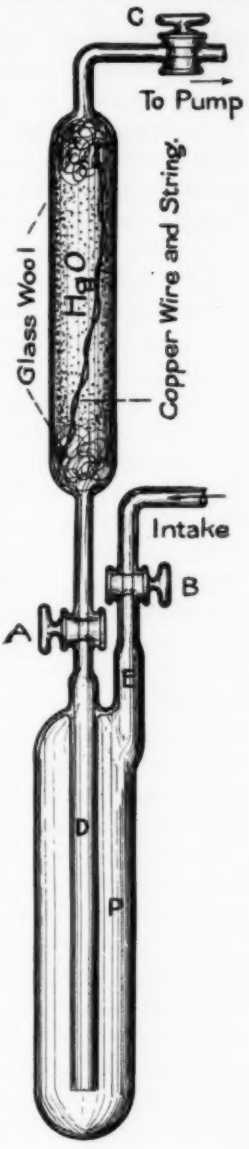


FIG. 8.—Apparatus for absorption of oxygen.

phorus vapor very satisfactorily if exposed to light. The literature ascribes an appreciable oxygen pressure to mercuric oxide under these conditions, but we find that this bulb pumps down and remains down even when exposed to light, and we also find that it does not stop phosphorus vapor if the mercuric-oxide tube is protected from the light. Since the tube seems to work quite as well by lamplight as in daytime, the reaction must be fairly sensitive.

Experience shows that it requires about three passages of the gas through the phosphorus bulb to insure the complete removal of the oxygen, and this is always done. It greatly slows the analysis but is unavoidable.

It is to be noted that here, as with all stopcocks in the analytical section of the apparatus, they are buried under mercury, as will be described farther on. The only essential is that in the disposition of phosphorus tube *P* it shall be so placed as to permit its being surrounded with a mixture of chloroform and carbon-dioxide snow at the close of the pumping. The actual operation is somewhat as follows: The gas is passed into bulb *P* and stopcock *B* closed; after three minutes or so, cock *A* is opened and most of this gas passes up into the mercuric oxide; cock *A* is closed and cock *B* opened to allow the next portion of gas to enter the phosphorus bulb. Cock *C* is then opened, allowing the gas from the mercuric-oxide bulb to pass back into the pump on its way to the volume bulb; *C* is closed, *A* opened, and after the gas has entered, *A* is closed again. The next portion is then allowed to enter *P* through cock *B*. This operation is continued, meanwhile pumping the gas from the pump over into the volume bulb. When the pressure of the gas at the intake side of *B* has fallen to a low value, it can be roughly estimated from the height of the mercury in the mercury trap in line *25* (Fig. 11), *AD* of Figure 20. The gas collected in the volume bulb is, without measuring, passed again into the intake side of *B* and the operation repeated. At the close of the third passage—or more if the indications of the phosphorus bulb suggest the need—the gas is passed and pumped down to about 2 centimeters pressure, i.e., the vapor pressure of water in the bulb *P*. *P* is now surrounded by the freezing-mixture and the pumping continued until the pressure is reduced to not more than 0.003 millimeters. This seems to be the most comfortable working

pressure for the phosphorus bulb, though it can be pumped down to the standard 0.001 with, however, some loss of time. If *P* is always pumped down to the same figure, the error introduced will not be large enough to be disturbing. With very small initial quantities of gas it will be necessary first completely to evacuate *P*—surrounded, of course, by the freezing-mixture—before making this absorption, and then reduce the pressure to 0.001 at the close. With reasonable initial quantities of gas, say 5 or 6 cubic centimeters, one may save time by raising the allowable pressure for *P* to 0.003. When this "complete" pressure is reached, cocks *A* and *B* are closed, and the by-pass cock (*22* of Fig. 11) between the absorption and the pump sides of the apparatus opened. Pumping is then continued until the pressure falls to 0.001 millimeters, after which the volume is read in the volume bulb. Opening this by-pass is merely in order to make sure that there has been no clogging of the passage anywhere in the train. Usually it produces no change of pressure; if it does, something needs attention.

Hydrogen

In this work one gets out of one difficulty only to find himself in another. When we have removed the sulphur dioxide, oxygen, and carbon dioxide, we have next to consider the separation of hydrogen, carbon monoxide, and possibly methane. In ordinary practice, these gases may be burned separately by the use of suitable catalysts. Since, however, these catalysts introduce manganese into the system and manganese cannot be admitted to this system, this nice procedure must be laid aside. There is no suitable absorbent for carbon monoxide. Even in the ordinary gas analysis, its determination is never beyond doubt, whatever the method used. Explosion or combustion of all three of these gases involves entirely too much uncertainty. We were therefore moved to try separating the hydrogen by diffusion through a palladium test tube, hoping to leave the methane and carbon dioxide behind. At the temperature used, this diffusion, while slow, is entirely satisfactory, as repeated tests have shown.

When CH_4 and its relatives are known or found to be absent, the procedure is simple. The mixed gases are merely passed over hot copper oxide and burned. From the contraction the amount of

hydrogen can be read, and a passage of the gas through the KOH bulb will yield the carbon monoxide directly. Any water formed will be taken up by the P_2O_5 bulbs.

The only difficulty here is the tendency of copper oxide to adsorb the gases and part with them slowly. Also it is known that at about 500° copper oxide begins to show an oxygen pressure. However, if the copper-oxide tube is exhausted at 400°, it may be subsequently reheated to 300° without appreciable development of gas pressure. As a matter of precaution, the copper-oxide bulb is always exhausted in this way before gas is passed into it, since upon standing for some days a small amount of gas may be evolved. It saves time if, instead of using the copper oxide of commerce in setting up the apparatus, one fills the bulb initially with pure copper wire or gauze and then oxidizes the surface of this wire by passing oxygen over it at about 400°. This procedure offers less opportunity for adsorptive disturbances, and the gauze can be easily reoxidized at any time if need be.

In practice, the copper-oxide bulb is exhausted at about 400° before each analysis, and the temperature is lowered to about 300°, where combustion will proceed readily and completely. The gas then passes back through the pump and into the volume bulb for measurement. It is necessary to give any gas some time in contact with its absorbent, so that gases are passed step-wise, as described in the oxygen determination. About 3 minutes per portion is sufficient, and the ordinary egg-timer or sand glass makes a convenient time-measurer.

We have found it profitable to use silica tubes for holding these reagents which must be heated and evacuated. They may be connected to the glass of the apparatus either by the flange tubes or by the cement seal described elsewhere in this paper. A small resistance furnace supplies a controllable source of heat, and each such tube has its thermoelement to indicate the temperature. The use of silica is to be commended because it does not crack as glass often does, and also because it can withstand much higher temperatures should these seem desirable.

Methane

If CH_4 is present or to be sought, then the hydrogen must first be removed by diffusion through the palladium diaphragm. This

bulb takes the form indicated in Figure 9. *B* is a palladium thimble or a test tube of pure palladium about 30 millimeters long and 6 millimeters in diameter, and is welded to a similar size of platinum tubing. The reason for this is that it is almost impossible to seal palladium to glass because of the gas evolution which occurs at the seal. The bottom or open end of this metal test tube is sealed to a

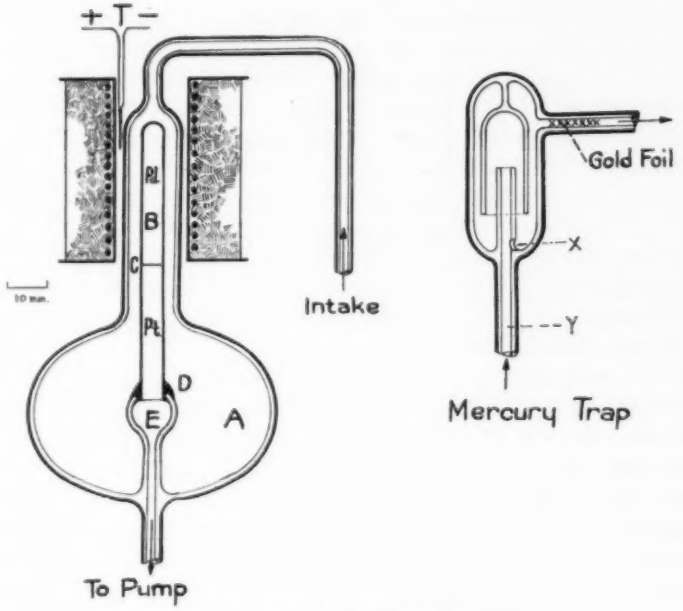


FIG. 9.—Apparatus for separation of hydrogen

glass tube *E* by means of the ordinary platinum sealing-glass. Tube *E* continues to the pump line through the usual stopcock, *A* is the containing-bulb for the gas from which the hydrogen is being extracted. It may have any convenient shape, but we have given it the one indicated in the sketch in order to have as large a volume as convenient and thereby to reduce the amount of gas left behind in the dead space, i.e., in the tubes from the volume bulb of the apparatus. The upper portion of this bulb is smaller and is situated in the small electric furnace, which is equipped with a thermoelement for control

of temperature. This arrangement allows bringing the palladium to about 200° C., at which temperature the diffusion is fairly rapid without danger of methane or carbon monoxide passing. The working-temperature is not a critical factor, and one uses whatever his particular arrangement shows to be most convenient.

It is better to insert a small mercury trap in both the intake and outlet tubes, since a drop of mercury rushing in against the palladium may necessitate removal of the tube and heating to drive off the mercury. We have used such a trap as indicated in the insert of Figure 9, though there is no necessity for anything so elaborate. The trap illustrated is so fashioned that drops of mercury caught by the bell can drain back down the tube *Y* through the opening *X*. We also inserted in the intake and outlet tubes either gold wire or gold foil to take up the excess of mercury vapor. In time, the palladium will take up enough mercury vapor to necessitate cleaning. This cleaning requires nothing more than removal from the bulb and heating in air to a good yellow heat. After such heating the palladium tube is best electrolyzed and tested for possible leakage, as suggested in the next paragraph.

A note on the treatment of these palladium tubes may be helpful. As obtained from the maker, they are practically inert to hydrogen, and also they may have concealed cracks between the rather coarse crystals of this metal. It is our custom to seal a new palladium tube to its glass base *E*, to heat the palladium to red heat in the flame, and seal it to a pump. It must not leak even when heated red hot. If the tube proves tight, it is then made electrode in dilute sulphuric acid, using alternating current for several hours. This activates the tube, and it may then be placed in its container and set up. Naturally after such treatment it will have to be pumped free of absorbed hydrogen.

In case of a leaky tube, there is nothing to do but return it to the maker to be remade. If the manufacturer understands that the tube is to be vacuum-tight, he can readily make it so.

We have tried a tube of an alloy of 65 per cent palladium and 35 per cent silver, which is said to absorb hydrogen even better than palladium,[1] but the results were not satisfactory.

During the construction of this absorption bulb it pays to check

[1] Sieverts, Jurisch, and Metz, *Zeits. anorg. Chem.*, Vol. XCII (1915), p. 329.

the tightness of all joints and the permeability of the palladium at each step.

The method is slow and the preparation of the tube may seem a bit troublesome, but it is no more so than other parts of the work, and it gives satisfactory results.

The actual analysis is carried out as follows: From the volume bulb the mixed gases are passed into the absorption side of the apparatus and the cock into *A* is opened; always, with all tubes in this apparatus, one first tests the vacuum of the absorption tubes at their working-temperature before leading any gas into them. In the meanwhile the furnace around *A* has been raised to 200°. The cock leading from *E* to the pump is also opened. As the pressure in the pump begins to rise, a low level is maintained by occasional turning over of the pump, forcing the transfused hydrogen over into the volume bulb. When after an hour's standing no further increase of pressure is noted, the hydrogen is brought into the volume bulb and measured. It is then passed out of the volume bulb into one of the small storage bulbs connected to the volume-bulb outlet and retained for further study. The gas from *A* is now pumped through the by-pass cock into the pump and on into the volume bulb and measured. The two volumes must of course check. It will now be wise to return this gas to the palladium tube for further diffusion, in order to make certain that all of the hydrogen, including that which was in the dead space between the volume bulb and *A*, has been diffused through. Usually this requires but a relatively short time. Any hydrogen which comes through is of course measured and transferred to the storage bulb with the main portion.

The residual gases are again brought into the volume bulb and measured. A sufficient amount of pure oxygen is now introduced into the volume bulb and the volume again ascertained. The gas now passes into the silica combustion tube, where the methane and carbon monoxide are burned. From there it passes back into the volume bulb and is again measured. It then passes to the KOH tube, and the CO_2 formed is determined. It then passes to the phosphorus bulb, and the residual oxygen is determined. From these readings the amounts of carbon monoxide and methane can be computed in the usual way.

The combustion tube used in this process is merely a silica-glass

tube electrically heated to about 800°. It is filled with chips of silica glass to supply plenty of reaction surface. There should now remain for determination only nitrogen and the rare gases.

Nitrogen

Nitrogen is easily determined by absorption in metallic calcium. It is perhaps the most satisfactory determination in the series. For this purpose an electrically heated tube of transparent silica is used, in which is placed a cylinder of metallic calcium. The tube is indicated in Figure 10. A clear (preferably) or well-glazed silica tube about 1 centimeter in internal diameter is drawn down and a small lead-in tube sealed to it. Some chips of silica are added to support the calcium cylinder, and then the other end of the silica tube is drawn down and the outlet tube sealed to it. The inlet and outlet tubes are joined to the glass tubes by means of a cement seal covered with mercury, as illustrated in Figure 25.

Stopcock *I* leads to the pump, and stopcock *F* connects to the absorption side of the apparatus. Between the joint *H* and stopcock *I* it is well to add a side tube which passes through the mercury-covered stopcock *A*. This in turn leads to the Pflücker tube B, thence to another mercury-covered cock *C*, which connects with a KOH tube *D* and the charcoal tube *E*. Tube *D* may consist of two bulbs; the one next to the charcoal contains KOH and the other P_2O_5. This side train is useful if the rare gases are to be further studied. Usually with gases from rocks the amounts will be too small to warrant the attempt at separation, and the argon will be so overwhelming that it will mask the lines of the other gases present.

The calcium tube is surrounded by an electric furnace which permits a temperature of about 700° and has a thermoelement for temperature control as indicated.

We have prepared the cylinders of calcium as needed, since it is necessary to have fresh, clean metal, and the calcium lumps and turnings on the market are practically useless, because of oxidation. Since calcium as purchased always contains a great deal of gas, mostly hydrogen, and the surface will unavoidably be covered with hydroxide during the necessary glass-blowing, such a tube must be heated and exhausted before it can be used. A temperature of about

700°, i.e., a little below the melting-point of the metal, works very satisfactorily.

Absorption proceeds very rapidly, and after it is completed the

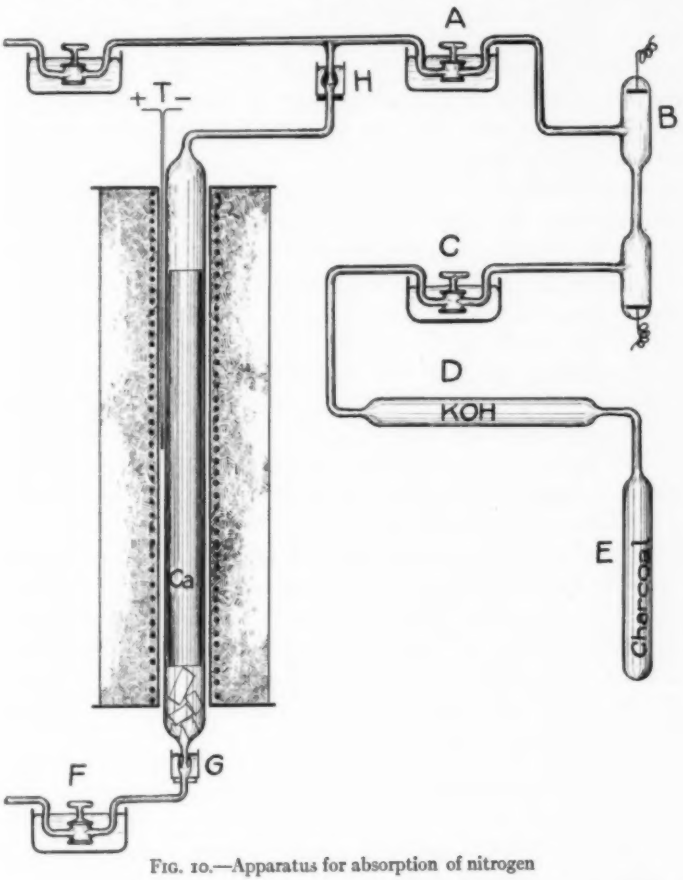


FIG. 10.—Apparatus for absorption of nitrogen

residue is pumped over into the volume bulb and measured. It is usually very small, a few hundredths of a cubic centimeter. With vacuum tubes containing air, it may be a little larger, and of course in special cases it may be significant.

Argon and the Rarer Gases

It is assumed that after the calcium tube, the residue is wholly made up of argon and the rest of that group. After measuring, the residue is again passed back into the calcium tube and the cock *A* of Figure 10 opened. The spectroscope can now be applied if the amount of gas is not too small. If there is too little gas to operate the tube, it is well to surround the charcoal bulb with a mixture of chloroform and carbon-dioxide snow, thereby absorbing the gas. After absorbing the gases into the charcoal in this way, the cocks are closed and this gas is left in the charcoal until another portion can be obtained from the next analysis of the material. The combination of the residues from a series of such analyses will sometimes permit some slight separation and identification. With gases from rocks, however, the amounts are usually too small, and a special study of these gases would be better than trying to work with the very small amounts obtained in the usual course of the analysis. It should be noted that if complete absorption of the rare gases by charcoal is desired, the tube should be surrounded with liquid air.

The separation and identification of these rare gases has been well described by several investigators, notably by Thorkelsson,[1] to whose paper the reader is referred for details.

If now the analysis is happily concluded, we may if necessary return to the diffused hydrogen which we left waiting in storage. This hydrogen should be returned to the volume bulb, measured, and then burned in the copper-oxide tube. After burning, the residue, if any, should be tested for CO_2. Unless there is a leak in the palladium tube, there will be no residue, and this burning of the hydrogen is merely to check the action of that tube.

DETAILED DESCRIPTION OF APPARATUS FOR THE ANALYSIS OF THE FIXED GASES

This apparatus works on the Orsat principle, with two essential modifications, namely, solid reagents are substituted for the usual liquid absorbents, and the gas is moved about through the apparatus by means of a mercury pump instead of being pushed about by

[1] T. Thorkelsson, "The Hot Springs of Iceland," *Mém. de l'Acad. des Sci. et Lettres, Denmark. Kong. Danske. Vedensk. Selsk.* (7), Vol. VIII (1909–11), p. 181.

the liquids. It is quite impossible to move gases quantitatively by displacement with any liquid. Even with the pump, certain gases, notably SO_2, tend to adhere to the tubes. We have used the method of measuring the pressure while holding the gas at a known volume, as is recommended for all exact gas measurement. If these facts are kept in mind, the apparatus is quite easily understood, however complex it may appear in the diagram. The complexity is entirely in the various attachments which experience has shown are helpful in the handling of the gases. Each investigator will add or subtract other features according to his special problem or method of manipulation. Some alterations or rearrangements are obvious, but it has been our endeavor to keep the apparatus to such limits as can be more or less easily constructed in any laboratory.

The Process

Perhaps the easiest method of description will be to follow a gas through an analysis, describing the various parts of the apparatus as they are brought into use. In the diagram (Fig. 11) those tubes which contain mercury are lettered, while those through which the gas passes are numbered. We have represented the apparatus as set up for determining the gases evolved from rocks *in vacuo*. Stopcocks are indicated by a crossed circle. Keep in mind the fact that the diagram is not at all to scale. Gas evolved in *2* passes through the Na_2CO_3 tube *4*, the P_2O_5 tube *5*, the silver tube *6* (when used), the small reservoir tube *7*, the P_2O_5 drying-bulbs *8* and *8''*, and into the pump bulb *9*. From the pump bulb it passes into the collecting-bulb *10* and ultimately into the measuring or volume bulb *11*. From here it passes through the three-way cock o into the intake side of the absorption system. It can then be passed through any of the reagents as KOH (16), or if need be through the by-pass *22* into the pump side of the system and pumped back into the volume bulb *11*. This operation is repeated until the analysis is finished.

Apparatus Details (by Number, Figure 11)

1 is a ruggedly constructed platinum-wire furnace capable of giving a temperature of 1,600°. The internal diameter is 5 centimeters, the length about 30 centimeters. For convenience the furnace is

mounted in a carriage which runs on a short track. This permits adjusting the furnace to the tube or its removal for purposes of chilling the tube. We are using the original type of furnace, inside wound with heavy platinum wire, as described in the earlier publications of this Laboratory. This is rather more rugged than the coils wound on alundum tubes, and stands the unavoidable battering which results when the silica tube collapses and wedges itself into the furnace.

2 is a silica-glass tube as supplied by the Thermal Syndicate. This tube is about 3.5 centimeters in internal diameter, 2 millimeters in wall thickness, and glazed inside and out. Its length is about 400 millimeters. These tubes vary considerably in actual dimensions and occasionally prove leaky, but for the most part have served admirably. Under vacuum they slowly collapse if the temperature rises much above 1,200° for any length of time. They are sufficiently translucent to allow some observation of the behavior of the charge within. Before placing the charge in position, the silica tube itself must be heated up to a temperature above that at which it is to be used, and exhausted until no more gas comes over. This detail has been uniformly ignored hitherto and is quite important. Calculated to our standard (1,200° and 760 millimeters), such a tube even after being heated to 700° in air gives off about 66 cubic centimeters of gas, of which the following is a typical analysis:

	Per Cent
CO_2	4.079
CO	3.936
H_2	0.192
N_2	0.008
H_2O	91.784

A Jena combustion tube of similar dimensions gave a total of 43 cubic centimeters of gas, calculated at 1,200° and 760 millimeters, when heated to its softening-temperature. We did not analyze this gas, since our interest in it was confined to demonstrating its presence. It is well known to makers of lamp bulbs or X-ray tubes that water and gas can be pumped either out of or off from any glass surface as the temperature is raised. This evolution of gas continues more or less indefinitely, but at any one temperature the surface can

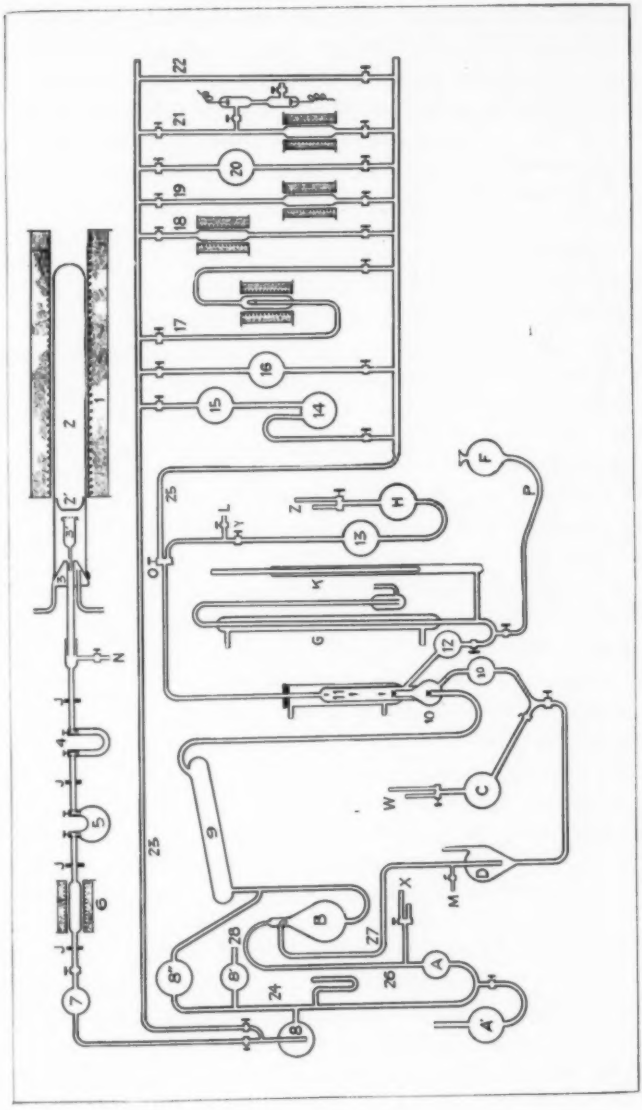


FIG. 11.—General diagram of apparatus for determination of the fixed gases

be exhausted sufficiently to avoid any error in analytical work. If, however, one raises the temperature higher than that at which the tube was exhausted, a fresh evolution of gas, including water, will manifest itself. This behavior applies to all adsorbed vapors when surfaces are to be freed from adherent gases. Therefore one must always evacuate the container at a temperature higher than that at which it is desired to maintain a vacuum. On the other hand, we find that an inert gas, that is, one which does not react with the reagent—as for example N_2 passed over CuO—while rapidly adsorbed at first, pumps off again if the temperature is kept steady. With finely divided or highly adsorptive materials, as for example PbO_2, while this adsorbed gas can be pumped off again, it may take considerable time to do it. Such highly adsorptive reagents should be used in as small quantities as possible, preferably spread as a thin layer over inert surfaces.

2′ is a reflector to screen the radiant heat from the plug at the end of the silica tube. A shield of platinum or a platinum crucible serves, though it will be contaminated with silicon as observed above.

3′ is the $CaCO_3$ tube described on page 316.

Previous investigators for the most part have placed the specimen to be evacuated in a platinum boat in order to save the silica tubes. In our experience, this hardly pays. In any case, the boat must be evacuated to free it from gases. Usually it is better to place the broken chips of rock directly in the silica tube. Even in 24 hours and with a basalt, the amount of silica taken up by the molten mass is unimportant, if indeed it can be detected. Nearly always if the rock is heated high enough to get out most of its gas, it will froth over onto the silica tube, and so the tube will be lost anyway. The boat seems a needless expense and nuisance.

3 is a water-cooled hollow copper cone turned from a solid block of copper and, after assembling, heavily gold plated. Through the center passes the exit tube for the gases. This exit tube is part of the original block, the object being to avoid a joint inside the furnace, and at the tip of the cone. Some blocks of copper are found to be flawed with minute cracks, which are of course fatal. The inlet tube for the water reaches to near the bottom of the cone, and the

exit tube is taken off on the opposite side. The object is to avoid any dead space and insure thorough cooling. The lid of the cone can of course be attached with hard solder. The cooling water is started before the heat is turned on the furnace, and kept running until the silica tube is cool afterward. The glass adapter tube connecting the cone to the rest of the apparatus is attached with De Khotinsky cement in such fashion as best pleases the operator. We have had rather better results with the arrangement indicated in the sketch.

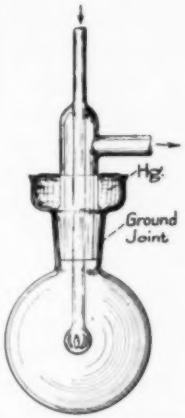


FIG. 12.—P_2O_5 bulb (*8* in Fig. 11).

N is a by-pass which allows evacuating the tube and charge without passing the products through the absorption train. It connects directly to a vacuum line.

J are flange tubes. This type of connection for vacuum apparatus was developed by Guye. The dimensions of the usual flange tube are given in Figure 13. We have found them useful and have had them made up in various sizes and out of soft glass, pyrex, and silica glass. The flange surface needs to be well ground and flat. They are held together after greasing by means of small U-shaped spring slips. A ring of soft cement is run around the edges. After a run, the flame is brushed over the cement to soften it, and the flanges separated. They are cleaned first by gentle scraping, then with a cloth moistened with alcohol, and with chloroform. The tubes to which they are attached can then be weighed.

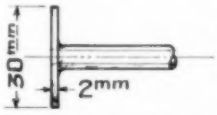


FIG. 13.—Flange tube

It has been found advantageous to seal into line, between the plug *3* and *J* of the Na_2CO_3 tube, a bulb which can be surrounded by CO_2 freezing-mixture. This bulb will catch and hold most of the water, any SiF_4, or HCl. The bulb is sealed off at the close of the run, the water weighed and analyzed. This allows us to eliminate the silver tube, *6*, for any rocks thus far examined.

4 and *5* have already been described in the section on gravimetric analysis.

6 is a tube containing silver gauze and surrounded by a small electric furnace which can be maintained at 200°. This is sometimes needed where H_2S or HCl is present in relatively large amounts. Chlorine or sulphur can be recovered by the usual methods. We seldom have use for this tube, but it may be necessary at times.

7 is a bulb of about 15 cubic centimeters' capacity which, when vacuum tubes are being analyzed, allows introducing a small amount of the gas into the volumetric system when desired. It also serves as a guard against leakage from the air in case the line goes wrong.

8 is a capacious P_2O_5 drying-bulb, so made as to allow renewal of the P_2O_5 without cutting the glass line; it is shown in detail in Figure 12. It also serves as a trap for errant globules of mercury, which will occasionally get out of control.

8′ is a P_2O_5 tube leading to the McLeod gauge. There is nothing unusual about this gauge, but in our experience a plunger tube for adjusting it is preferable to the air-vacuum adjustment. It is, however, desirable to use the extra P_2O_5 tube next the gauge in order to prevent moist air from entering the gauge, should an accident allow such to enter the system. These gauges must be kept dry and are difficult to dry out, hence the precaution.

24 is the main intake line into the pumping-system. It is closed at the bottom by a barometric seal, the bulb and U tube *A*. The object of this connection is to avoid a stopcock and at the same time to permit evacuating the system by means of the mechanical pump. This is done by drawing back the mercury from *A* into the bulb *A′* until the system has been exhausted, and then sealing this connection by admitting the mercury again through the cock between *A* and *A′* until enough mercury has entered the bulb *A*.

8″ is another P_2O_5 drying-tube which, while not absolutely necessary, is useful.

B–9 is the pump. This is one of the numberless modifications of pumps actuated by means of an auxiliary mechanical pump, which saves lifting the mercury and avoids fouling it with rubber connections. Bulb *B* (detail, Figs. 14 and 15) has 2 lifters' capacity and is so placed that the level of the mercury in it is about 6 centimeters lower than the intake tube of the pump bulb *9*. The mercury is manipulated by means of the stopcock *X*, one arm of which connects

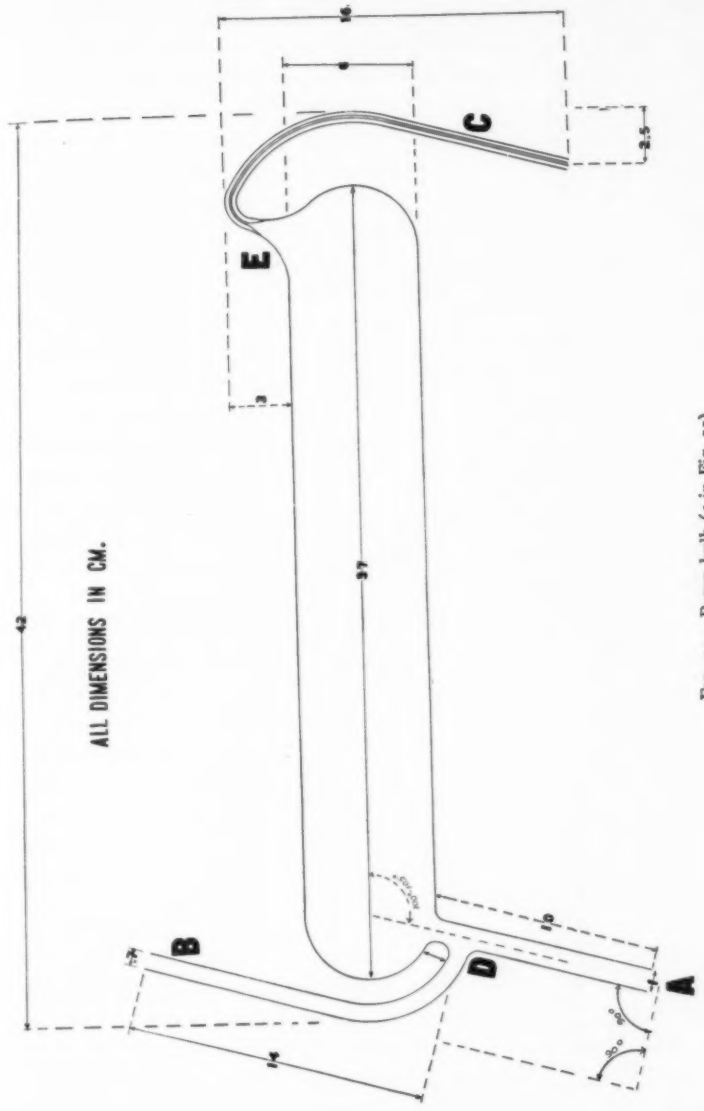


FIG. 14.—Pump bulb (9 in Fig. 11)

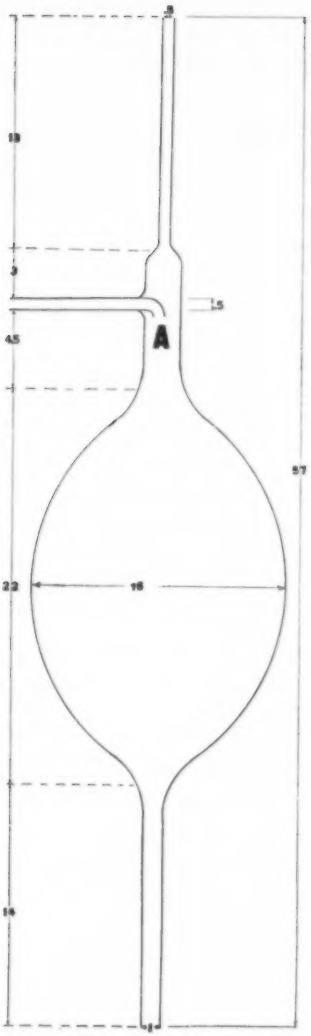
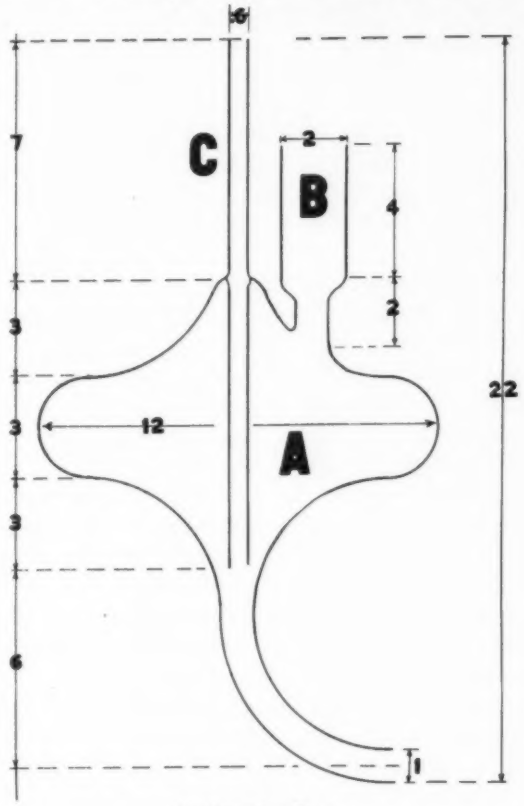


FIG. 15.—Reservoir bulb (*B* in Fig. 11).

to the mechanical pump for exhaustion and the other is open to the air. When the mechanical pump is thrown in, the reduced pressure causes the mercury to flow back from *9* into *B*. When *X* is opened to the air, the pressure raises the mercury into 9 until it flows over and into the collecting-bulb *10*. The line *27* is the elevator for raising the overflow of mercury from *10* back into the bulb *B*. The pump bulb *9* is of about 1 liter's capacity. Details of construction of both bulbs *B* and 9 are sufficiently indicated in Figures 14 and 15. In assembling the apparatus, be sure that the "riser" tube between *9* and *8''* is at least a meter long. A mercury trap in it will be helpful.

By opening the stopcock between 10 and *D*, the overflow of mercury into *10* is drained back into *D*. The difference in level between *D* and *B* is about 2 meters. If now with *B* exhausting we allow small bubbles of air to enter line *27* through the small cock *M*, a series of globules of mercury will be drawn up line *27* and the mercury fall into *B*. In this way the elevation is accomplished without difficulty. In fact, Pamfil worked out the system so that this elevation was continuous and made the pump automatic. We cannot advise such use, but it can be done until the apparatus

breaks, as it surely will. One unintentional benefit of this method of elevating the mercury lies in the cleansing action of the air on these globules of mercury as they rattle along up the tube. In time



All dimensions in cm.

FIG. 16.—Overflow bulb (*D* in Fig. 11)

the walls of the tube become quite dirty. The tube can then be cut out and cleaned, but the mercury in the pump will remain clean over several years. The cock between *D* and 10 is mercury-sealed and lubricated with graphite instead of grease. Line *27* is made of about 4-millimeter glass tubing. *D* should have about the dimen-

sions given in Figure 16. Its shape is based upon the desirability of allowing a relatively large change in volume with little change in "head," that is, mercury level.

C is a level bulb for managing the mercury in 10. It should be about 10 centimeters lower than the base of *10*. The mercury is moved by means of the cock *W*, one arm of which connects to the mechanical pump, the other opens to the air. By exhausting *C*, the mercury in *10* is drawn back, allowing the gas from 9 to expand into *10*. By turning *W* to air, the mercury rises, driving the gas up into the volume bulb proper. The volume of *C* is determined by the capacities selected for *10* and *11*. With our apparatus 300 cubic centimeters is sufficient.

10′ is a bulb of 500 cubic centimeters' capacity. When it is desirable to separate the gas into two or more measured portions, the second portion can be retained in *10–10′* at reduced pressure while the portion in 11 is measured and passed on into the machine.

10–11 is the volume bulb. This involves no new principle, but has been constructed on familiar lines (Fig. 17). In order to avoid passing gas and mercury through the same stopcock, we have substituted two platinum valves which close off the system from the pump while readings are being taken. Naturally such a bulb will be made in various sizes according to the amount of gas with which one expects to deal. Since we seldom have more than 10 cubic centimeters and often much less, our bulb has the dimensions indicated in the sketch. The burette is divided into four known volumes.

OA, the capillary tube at the top, is constricted at *O* to form the zero of the burette. Theoretically, the mercury thread breaks at the constriction, and with some patience it can be made to do so sharply even when the pressures become low. This mercury thread is adjusted by means of stopcock *O* (Fig. 11). At *A* (Fig. 17) a scratch or other indicator is placed on the capillary and the volume *OA* is calibrated with care. With our burette, the volume is about 0.08 cubic centimeters. It is, however, desirable to know the volume of this tube in terms of millimeters, since with the argon residues as obtained from rocks the amounts are so small that the use of the whole volume *OA* is not feasible, and mercury will creep down through the constriction. An old thermometer stem with gradu-

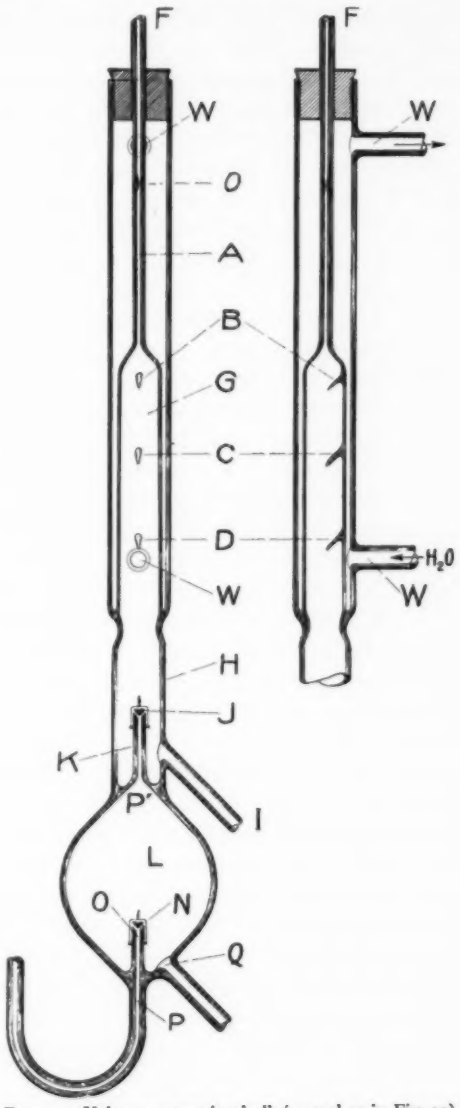


FIG. 17.—Volume-measuring bulb (*10* and *11* in Fig. 11)

ations on it would be very helpful at times if substituted for plain capillary in making up the bulb.

B, *C*, and *D* (Fig. 17) are points of black glass, as usual with such burettes. They should be well centered and there should be no roughnesses at the point where they are sealed into the burette wall, since there is always a tendency for gases to lie down when one is passing them out of one bulb into another. To eliminate the correction for capillarity, the burette *G* is made of the same diameter as the barometer tube. It so happens that with our apparatus the volumes are *OB* 1.9, *OC* 7.6, and *OD* 13.7 cubic centimeters, respectively. The calibration of these volumes is done in the usual way, using mercury.

The water jacket *F* around the body of the burette is roomy enough to allow a rapid circulation of water and is closed at the top by a rubber stopper covered with soft cement. Our apparatus has a 25-millimeter tube for a water jacket, the intake and exit being indicated in the figure. This jacket is connected preferably to a thermostat, but by inserting a good thermometer in the water line one can read the temperature and make the necessary correction.

Bulb *L* (Fig. 17), which receives the gas from the pump, should have a relatively large volume as compared with the amount of gas it is expected to take. With our apparatus it is a bulb of about 200 cubic centimeters' capacity. It is necessary with a pumping-system of the type described to collect the gas at reduced pressure. Also there are occasions when one wishes to divide a specimen into two portions, and this can be done by passing part of it into *G* and then, after covering the valve *J* with mercury at a higher pressure, collecting the second portion in *L* at a reduced pressure.

Valves *J* and *N* are platinum valves which serve to replace the stopcocks which would otherwise be necessary at these points. The valves are made up as indicated in Figure 18. A small sphere of platinum is formed by melting the end of a heavy platinum wire. This wire serves to grip the sphere while it is being turned in the lathe and also in grinding the valve into position. A piece of capillary tubing, carefully annealed, carries, sealed to it by drops of the soft glass used for platinum seals, three fine platinum wires equally spaced around the circumference of the tube and about 1 centimeter from the end. By means of a brass cone and emery, the valve seat

is now roughed out in the end of this capillary tube. The platinum valve is then ground into place. The valve should sit a little below the level of the glass. We have found that an angle of about 60° for the cone of the valve gives good results. The platinum wire is now turned off from the valve, the valve and tube carefully cleaned to free them from débris and grease and put in position, and the platinum wires twisted down to hold the valve in place. These valves should be carefully tested before being used. They must not leak mercury under pressure and should be fairly tight when suction is placed on the tube.

FIG. 18.—Platinum valve for bulb *10* (Fig. 11).

Of course when the mercury becomes foul, the valves will no longer hold and the apparatus must be cleaned, since we are dependent on these two valves to hold back the mercury while the volume is being read. It is obviously important that the valves be not heated after being ground and that they be placed so that the junction of the valve with the adjoining glass is reasonably remote. Three or four centimeters will do.

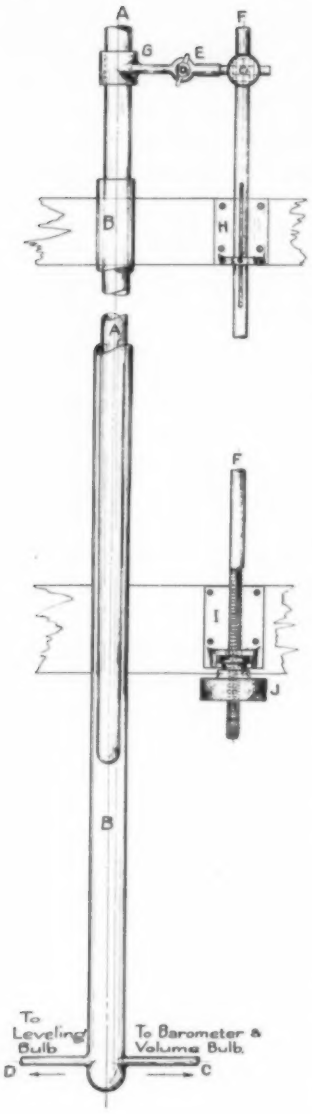
It is of course important wherever mercury and gas pass from one tube into another that the constriction shall be gradual and smooth as at *P* and *P'*.

H is merely an antechamber made necessary for convenience in assembling the apparatus and to allow the connection *I* to the barometer.

Q is the connection to the leveling-bulb *C* and the overflow bulb *D*.

The capillary *P* runs to the pump *9* of Figure 11.

Assuming that by proper adjustment of the mercury in the level bulb *C* of Figure 11 we have driven the gas into the volume bulb *G* (Fig. 17), stopcocks to *C* and *D* being closed, the stopcock connecting with the barometer *G* is opened and by adjusting the level bulb *F* the gas is brought to whichever volume is to be used. Having brought the mercury in the volume bulb to approximate adjustment, the stopcock connecting to *F* is closed and the fine adjustment, contact with the glass point, is made by means of the device shown in Figure 19.



B in Figure 19 is a large, well-annealed glass tube about 35 millimeters internal diameter and about 1.5 meters long. Since soft glass even when annealed tends to crack, we finally used such a tube made of Jena combustion tubing, in spite of the difficulty of making a good joint between this and the soft-glass parts of the apparatus. We made the barometer of Jena glass also, but that is not absolutely necessary. Where pyrex is used, these difficulties are avoided. Such a plunger tube must be straight and of fairly thick wall. Into this tube fits a plunger made by sealing one end of another straight heavy-walled glass tube. These two tubes must fit closely without binding, but a too tight fit is not desirable. This plunger is held by the clamp *E*, which in turn is mounted in the block *G* in such manner as to allow any desired adjustment of the clamp. *F* is a steel rod about 15 millimeters diameter, which is held in position to the frame of the apparatus by the two iron guides *H* and *I*. The rod *F* moves freely up and down through *H* except for a loose slot and pin which prevents it from turning on its axis. The lower end of *F* has a screw thread

FIG. 19.—Device for fine adjustment of mercury in the measuring-bulb (bulb *11* in Fig. 11).

cut on it and moves freely up and down through block *I*. Into *I* is set the adjusting nut *J* in such manner that turning *J* allows a fine adjustment of the rod *F* without danger of *J* becoming detached and falling, or of allowing the plunger to drop. The adjusting-nut *J* is placed within easy reach of the volume bulb so that one may watch the mercury meniscus with a lens while turning the nut.

At the bottom the plunger tube may have two tubes as indicated by *C* and *D*. One leads to the leveling-bulb *F* (Fig. 11) and the other goes to the volume bulb and barometer, there being a stopcock between *F* and the barometer system, and also between the barometer and the volume bulb. It is an improvement to omit the rubber tubing to the leveling-bulb *F* and manage this mercury by pressure and vacuum, but we have used the ordinary leveling-system.

12 is merely an expansion bulb. It is sometimes useful when the volume of gas to be handled proves unexpectedly large.

After the measurement of a volume of gas, the clamp *E* (Fig. 19) is released and the plunger forced down to put pressure on the gas in the volume bulb. The clamp is then tightened, and the stopcock *O* (Fig. 11) opened into whichever line one desires to pass the gas. In an analysis this means into line *25*. This passage from *O* to line *25* is made through the mercury trap *A* (Fig. 20), into which the gas passes by the re-entrant tube *B*, which causes the globules to pass downward into the trap instead of being carried over into the absorption side of the system along with the gas at *C*. We have found it useful to make this trap of the form shown in the sketch, the lower bulb having about 100 cubic centimeters' capacity and being distant from *A* about 10 centimeters more than a barometric height. This allows one to observe the rate of absorption and otherwise keep watch on the gas. The side tube *E* allows draining off the mercury from time to time. Also one can attach a rubber tube to *E* and by blowing or sucking on this manipulate the gas to advantage. Bulb *A* has a volume of about 10 cubic centimeters, though as long as the volume is kept small without hindering the collection of the mercury globules in *D*, the exact volume is unimportant.

The other passage from stopcock *O* is the outlet tube of the apparatus. This passes the stopcock *H* (Fig. 20), which need not be mercury sealed if it be well ground, to the small reservoir *I*. One

keeps a small amount of mercury in this reservoir to protect the apparatus and also to be used in adjusting the upper mercury level of the volume bulb at *O* in Figure 17. *J* (Fig. 20) is a valve-stopper similar to those on the ordinary drying or absorption tube. This can be closed to protect the mercury when not in use. When it is open and cock *H* open, one can allow the mercury thread in the

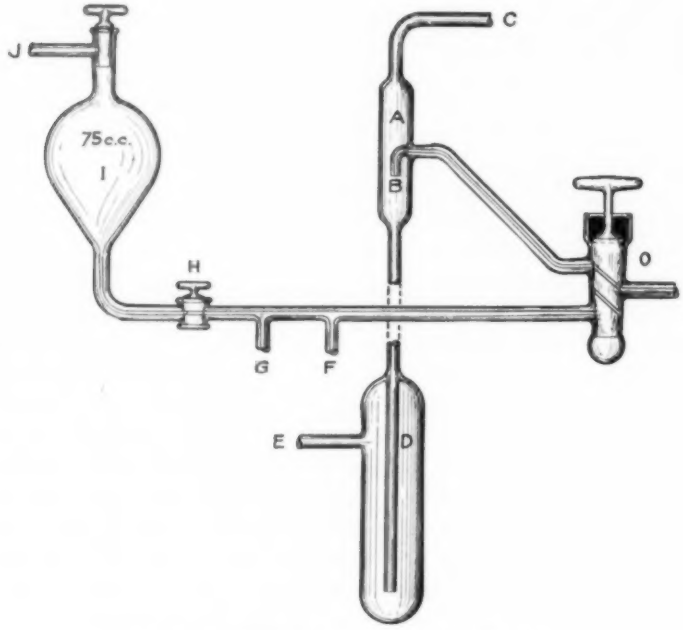


FIG. 20.—Connections at the stopcock *O* (Fig. 11)

volume bulb to flow until it reaches *O* (Figs. 11 and 20). If zero is passed, it is easy to apply suction to *J* and draw the thread back to *O*. Except for this adjustment or when emptying the volume bulb, *H* is kept closed.

The two taps *G* and *F* allow one to arrange for a reservoir for gas to be analyzed in the case of large vacuum tubes; thus bulbs *13* and *H* of Figure 11 are manipulated by the cock *Z*, one arm of which connects with the mechanical pump, the other being open to the air

to allow the mercury to force the gas back into the analyzing system. The other tap, as *F* (Fig. 20), leads by suitable stopcocks to reservoirs for storing small amounts of gas and to the oxygen-generator if it be desired to introduce oxygen for purposes of combustion. The system *O* to *F* to *J* of Figure 20 corresponds to *O*, *Y*, and *L* of Figure 11. Such side tubes are always attached to the under side of the horizontal mains, and in this part of the system are of capillary tubing, special care being taken that the T joint shall be smooth and leave no place for gas to collect. Even with capillary tubing, gas shows a decided preference for clinging to the glass and allowing the mercury to pass over it.

Barometer *G* is shown in Figure 11, and in detail in Figure 21. At the time our apparatus was assembled, pyrex was not available, and because of the tendency of ordinary soft glass to crack, we made the barometer of Jena glass. The tube itself, *A*, is 1-centimeter tubing—the same diameter as the volume bulb—and is water jacketed (*B*). This water jacket connects directly with the water jacket of the volume bulb, in order to eliminate temperature correction. The lower end of the barometer takes the S-shaped form *D* in order to avoid excessive convection currents in the mercury, and has the air trap *E*, which may be either a small tube which can be sealed off or a particularly good stopcock. This is very useful in managing the mercury from time to time. The extension continues to the plunger tube shown in Figure 19. The upper end of the

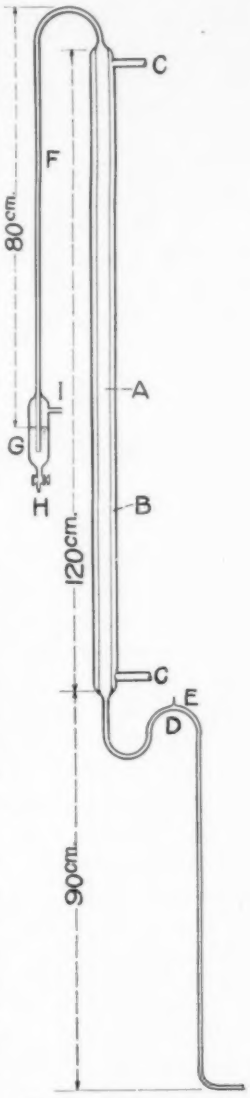


FIG. 21.—Barometer tube (*G* in Fig. 11).

barometer tube is drawn off smoothly to connect with the capillary tube *F*. This tube *F* is 80 centimeters long, and the lower end dips into the mercury trap *G*. For convenience, *G* may have a stopcock *H* for draining off overflow mercury. The side tube *I* permits exhausting the barometer in filling, and we have usually followed the procedure of running the mercury over the top again before starting a series of determinations.

The barometer tube being more than an atmosphere of mercury in length, it is necessary to exhaust through *I* and raise the mercury by means of the plunger. Since one cannot flame the barometer tube in drying out the apparatus, one is compelled to fill the jacket with warm water and then exhaust through a P_2O_5 bulb before forcing the mercury over into *G*.

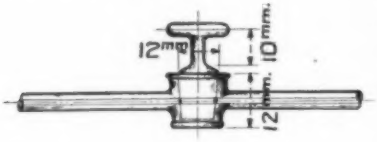


FIG. 22

For reading the barometer, any convenient system may be used. We have with our apparatus used a glass mirror scale placed behind the barometer. This is sufficient in most cases, but any degree of refinement may be added, depending upon what the apparatus is supposed to do. It is, of course, necessary to establish the relation of the index points of the volume bulb to the scale. This can be done with a cathetometer. A cathetometer can of course be substituted for the scale, but all of them are bulky and little suited for use in a chemical laboratory. It would be highly advantageous if one used a scale of, say, 1.5 meters, which would permit handling unexpectedly large amounts of gas.

The next position for the gas is in the absorption side of the apparatus, that is, line *25* of Figure 11. From this line the gas is passed into its proper absorption tube by opening the proper stopcock. When desired, the gas may be passed directly to the pump side, line *23*, by stopcock and line *22*, referred to as the "by-pass."

Stopcocks

There are few if any stopcocks which do not leak; and there is none which will not develop leaks if exposed to changing tempera-

tures. We were finally driven to bury all essential stopcocks in mercury. Nor have we found the mercury-sealed stopcocks of any special merit. Always, all of them must be reground with care. The most

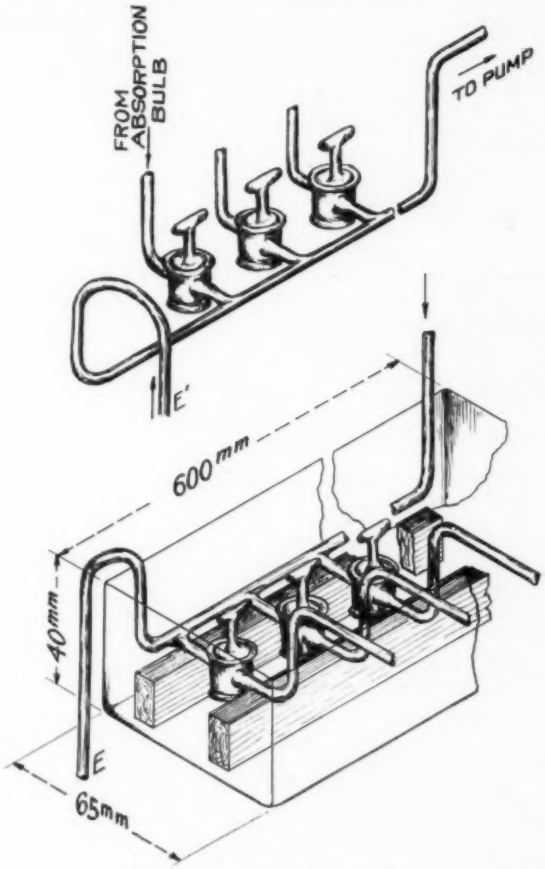


FIG. 23.—General arrangement of stopcocks leading to absorption bulbs

satisfactory in our experience are small stopcocks of the dimensions shown in Figure 22, with about 1-millimeter bore. These can be readily buried under mercury and will then hold for more or less

indefinite periods. From time to time it will be necessary to pipe off the mercury and clean and regrease the plugs, care being taken that the grease does not stop off the tubes.

Figure 23 shows the general arrangement of these stopcocks. The main line (25 in Fig. 11) dips under the mercury in the trough and slants gently to the end, where the tube *E* (Fig. 23) serves as a small mercury trap and also permits getting into the apparatus for sealing or blowing when repairs are needed. *E* turns over the side of the trough and is drawn down to a sealed tip. A few more cocks than there are absorption bulbs are sealed into the main line (25) to allow for further additions of absorbents should such be needed. This array of leads and cocks is submerged and anchored in the trough as shown in the detail sketch of Figure 23. The trough is made of sheet iron welded at the corners, and has the approximate dimensions 40×60×600 millimeters. To the bottom of this are anchored two strips of wood so placed as to allow the stopcocks to be firmly set by small sheet-iron strips screwed to the wood (Fig. 24). In assembling, these wooden strips should be a few millimeters higher at the upper end, so that errant globules of mercury will collect near tube *E* rather than next the stopcocks.

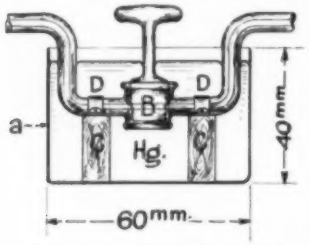


FIG. 24.—Method of mounting stopcocks in mercury trough.

The upper trough is similar in construction except that its main line runs to the pump intake, and the tube *E'* (Fig. 23) is the bypass 22 (Fig. 11). These two troughs may be arranged in any manner which proves most convenient. On our apparatus they are placed one above the other, separated by a clear space of about 40 centimeters. This allows plenty of room for the absorption bulbs and for the unavoidable glass-blowing necessary when a reagent is to be renewed.

The absorption bulbs for oxygen, nitrogen, hydrogen, and sulphur dioxide have already been described.

Figure 27 is a diagram approximately to scale to show the disposition of the parts of the apparatus. Figure 28 is a photograph of the apparatus as used.

THE ASSEMBLED APPARATUS

Unless otherwise specified, all references in this section refer to Figure 27. This drawing is made to scale with the exception of the reagent bulbs, which have been slightly enlarged. This variation is unimportant, since these bulbs will be constructed and disposed according to the preferences of the operator. As a matter of fact, our apparatus has been more or less wound around and interlaced with the supports, depending on convenience at the time. The essential feature of this figure is the relative positions of the various bulbs and tubes. These values may be obtained by measurement on the figure.

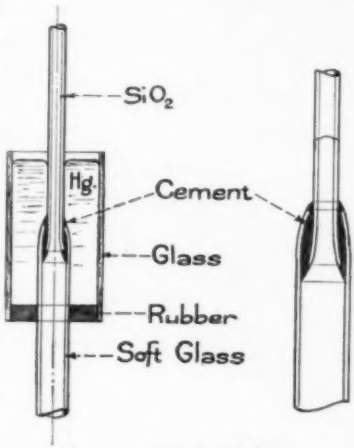


FIG. 25.—Cemented joints

Capillary tubing is indicated by solid lines.

1 is the intake from whatever source or sources may be desired. With our apparatus, this intake connects to a series of stopcocks which allow it to be connected either to the furnace or to the auxiliary mechanical pump line as desired.

FIG. 26.—Type of U tube with nipple.

2 is a stopcock which connects with the return line from the reagent bulbs. Both stopcocks, *1* and *2*, are obviously of critical importance. They must be carefully ground and buried under mercury.

Gas entering from either of the above lines passes first through the P_2O_5 bulb and thence into the vertical line leading to *4*, *5*, and the pump bulb *7*. At the bottom the vertical line is closed by the mercury barometric seal, which is controlled by bulbs *20–22* and stopcock *21*. This stopcock *21* needs to be of good quality, but since both leads to it are kept full of mercury, it need not be a buried one. If very large quantities of gas are to be handled, the seal must of course be of barometric height on both sides of the U. Such quantities, however, cannot be handled properly by a pump arranged as

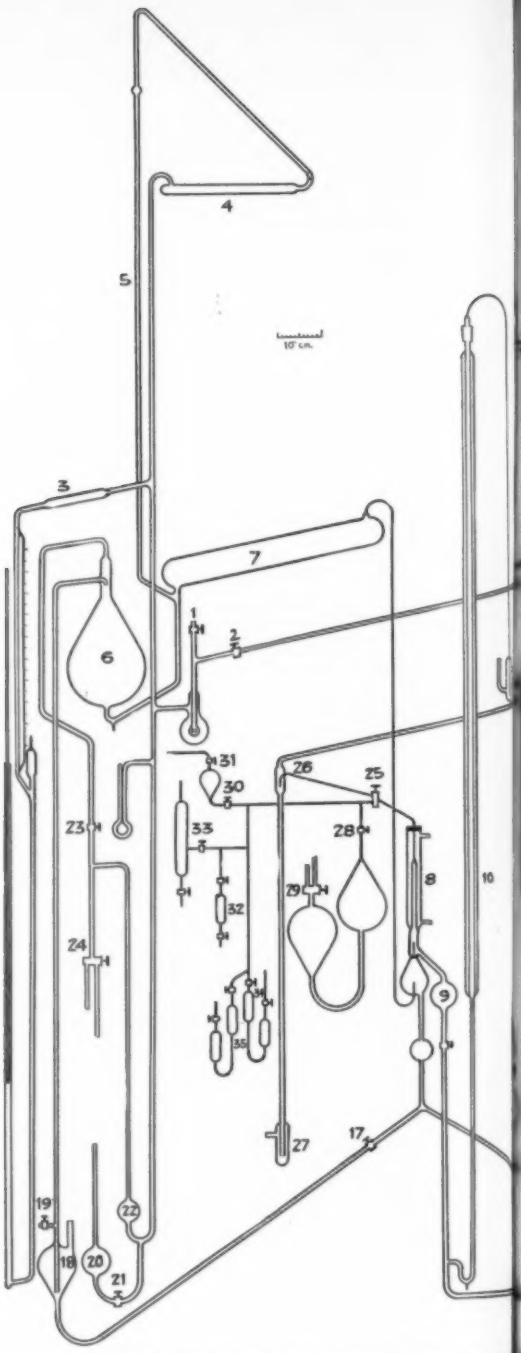
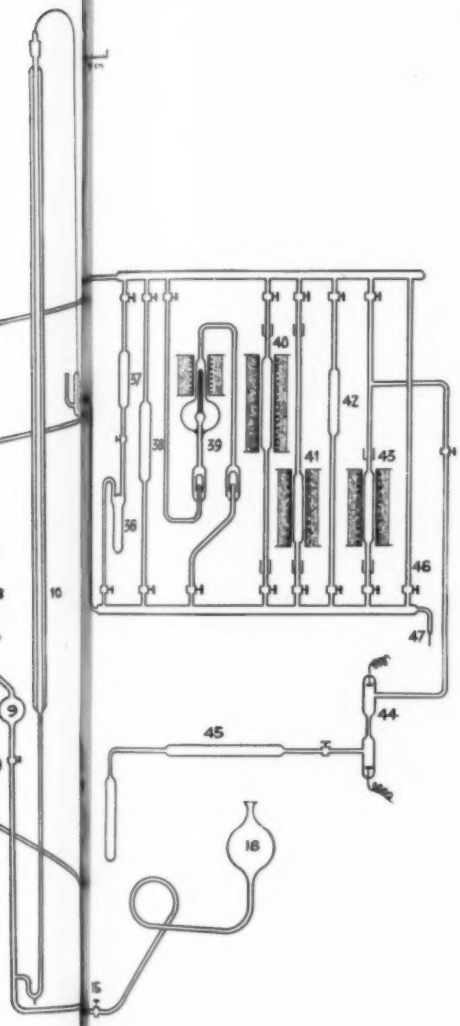


FIG. 27*a*.—General layout of the apparatus, drawn to sc



drawn to sc

7b.—General layout of the apparatus, drawn to scale

this one is, and so the U need not be more than about 20 centimeters high.

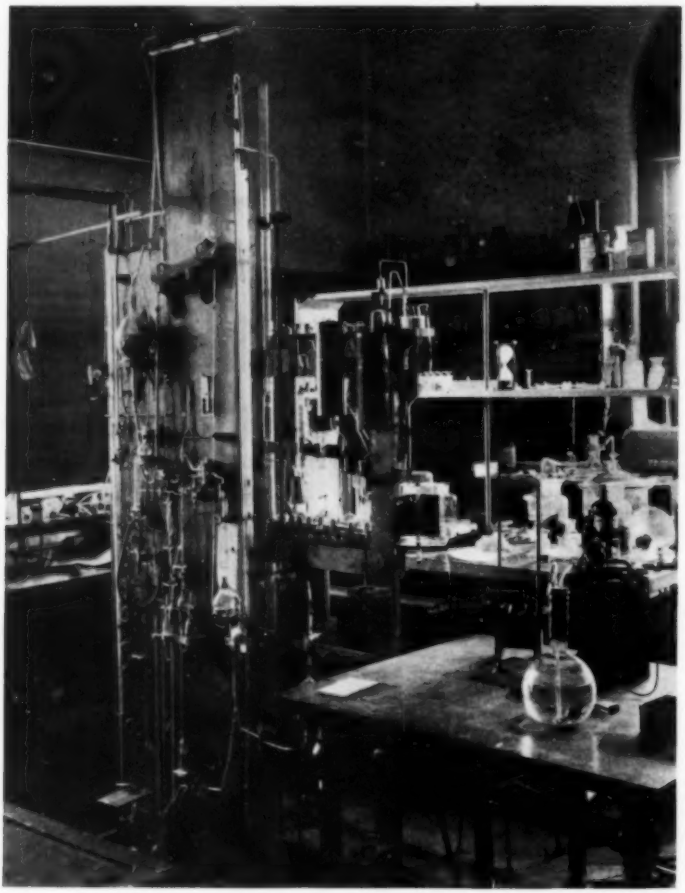


FIG. 28.—Photograph of assembled apparatus

It is a convenience to have an ordinary manometer sealed to the vertical line as shown, and also to connect to it through a P_2O_5 tube, *3*, the McLeod gauge.

It will be noted that the total height of the vertical line is about 3 meters, and more does no harm. Obviously the intake to the vertical line must be more than 1 meter above *22*, and the vertical line *5* must extend a good 1.5 meters above the intake to the pump bulb *7*.

The tube connecting the pump bulb *7* with the reservoir *6* may be any desired length or size. A U somewhat longer than the one illustrated prevents loss of gas should there be momentarily too great pressure entering the line. On the other hand, the longer the U, the slower the pump will operate.

From the pump the gas passes down the capillary into the volume bulb *8*.

8, the volume bulb, connects via *9* and a stopcock with the barometer, *10–11*, and the leveling-devices, *14*, *15*, *16*.

10, the top of the barometer, leads down the meter-long capillary to the trap *11*.

12 and *13*, along with the bulb in the line between them and the collecting part of the volume bulb, are used to manage the mercury and gas for this part of the system. Stopcock *17* allows draining off the mercury from this part of the system back into the elevator and pump reservoir.

From the volume bulb *8* the gas passes through stopcock *25* in either of two directions as desired. (This is stopcock *O* of Fig. 11.)

It may be sent into the large storage bulb *28–29*, the smaller storage bulbs 35, the line for determining SO_2 by titration, 33, or out of the apparatus, 30–31.

The second and usual path for the gas is through *25* into the mercury trap *26–27* and on to the absorption bulbs.

The absorption or reagent bulbs here indicated are: *36*, yellow phosphorus; *37*, mercuric oxide; *38*, KOH; *39*, palladium diaphragm for separating hydrogen; *40*, cupric oxide; *41*, combustion bulb where oxygen is used; *42*, lead-peroxide foil for sulphur dioxide; 43, metallic calcium for nitrogen absorption; 44–45, Pflücker tube and accessories for argon, etc.

47 is the sealed-off end of this line, which may be used either for draining off mercury globules or for glass-blowing during repairs

46 is the by-pass whereby gas may be returned to the pump without passing through any of the reagents.

18 is the overflow bulb into which is drained the excess mercury from the volume bulb. From *18* the mercury is elevated to the reservoir bulb *6* by proper adjustment of stopcock *19*.

One outlet for stopcock *24* connects with the mechanical pump, while the other is open to the air. This stopcock is the one used to work the pump. The additional stopcock *23* is not absolutely necessary, but has been found convenient.

There are a number of convenient additions which may be made to the system as sketched in this figure. For example, stopcock *31* and bulb *20* may be sealed by three-way stopcocks, so that they may be directly connected to the line of the mechanical pump. It is wise to omit the rubber tubing between *15* and *16*. In that case, *16* should be placed about level with the base of *8*, or about 1 meter above the base of the plunger tube; *15* placed directly under *16* and a three-way stopcock sealed to the top of *16*. One arm of this stopcock leads to the mechanical pump and the other remains open to the air.

There are a few minor details which might be mentioned as helpful. There are two kinds of joints which can be made easily as between soft glass and any other. These are indicated in Figure 25. Where no great pressure is to be considered, a simple union is formed by sliding one tube inside the other, and sweating De Khotinsky cement into the annular space between the tubes. This sweating must be done at a temperature low enough so that the cement does not boil. The outside is then neatly covered, and a suitable rubber stopper run up until it will hold a larger glass tube filled with mercury around the joint.

If for any reason the cement is regarded as undesirable, a ground joint may be made and the outside ringed with cement.

Where considerable pressure is anticipated, we have used the second type of joint shown in the sketch. In this case, the larger tube is drawn down to a cone and a somewhat smaller tube of the second kind of glass also drawn down to about the same angle. This smaller cone slips into the larger and the space between the two is filled with cement. It is now possible to buy silica-to-soft-glass and pyrex-to-soft-glass joints made up of a series of intermediate glasses, but the above expedients will serve quite well if these special joints are

not available. Where the cement is to be avoided as far as possible, it is also feasible to bring the two tubes of different glass but the same diameter sharply end to end and surround them with a splint made of a slightly larger tube, this joint also being filled with cement. This is obviously similar to the usual method, where rubber connections are used for two abutting tubes.

Since apparatus will break from time to time and also since fouling of the mercury necessitates occasional cleaning, we have found it wise to add a short nipple at the bottom of all U tubes containing mercury, as for example at the lowest point on the tube connecting the pump bulb and the reservoir *B*, Figure 11. In this particular case a short (1-centimeter length of 3- to 4-millimeter tubing is sealed to the bottom of the U. When it becomes necessary to empty the mercury, the tip of this nipple can be broken off and the mercury caught in a bottle. It is often sufficient merely to heat a small spot on the lower side of the U and touch it with a piece of glass tube and draw out a short nipple, as in Figure 26. These are minor details, but often help a great deal in cleaning and repair.

For all general gas-conducting lines we have used a soft-glass tubing of about 4 millimeters external diameter. This tubing is easily manipulated and elastic enough to prevent breaking from strains in the apparatus. It also permits bending the tube to any desired position by merely warming a section of it in the flame and twisting it into position. It is light enough so that it need not be supported in any great measure. Tubes through which mercury must pass should never be horizontally placed. A slight angle of not less than 10° is essential in order to permit driving all of the air or gas out of such tubes.

When the apparatus has been assembled and dried by drawing air first through a $CaCl_2$ tower and then through the apparatus for some hours, the whole apparatus is gone over with a gentle flame and each part heated while the dried air is passing through it. Finally the various sections of the apparatus are exhausted with the mechanical pump and the apparatus again flamed. Only by such a severe drying-out can the apparatus be cleared of adsorbed gases. Similar treatment is administered after repairs.

There are many sorts of stopcock grease described in the liter-

ature, and that given by Travers is as good as any. It should be remembered that a pure gum rubber must be used and the temperature of the mixture held to a minimum. Otherwise hydrocarbons will be released which will in use give the grease an appreciable vapor pressure. The grease we have used was given us by a colleague who was formerly in the employ of a corporation dealing with high-vacua apparatus. How it was made we do not know, but it is perfect in action, and colorless.

We have no great wisdom to impart in the matter of leaks. They occur anywhere and at any time. One can only search for them. Not infrequently they will be located at a joint, even though it may appear well sealed, and the simplest if not the prettiest way to search is to warm the joints one by one and smear them with soft De Khotinsky cement. Thus one eliminates one joint after another until the guilty one is located. It is easy to warm the joints and wipe off the cement if one wishes. Occasionally a piece of glass tubing is found which leaks and no source of the leak can be discovered. Since this apparatus depends so largely for its accuracy upon the absence of leaks, one has no choice but to keep checking and doctoring whenever necessary.

PART III

GENERAL CHARACTER OF THE RESULTS

SOURCES OF ERROR

The chief sources of error in these methods fall naturally into the two groups: those associated with the gravimetric procedure, and those implied in the gasometry.

In the gravimetric section we have been at some pains to indicate the main weaknesses of the methods adopted. As far as these errors affect the final result, we have no alternative to offer. Fortunately, these errors need not be serious enough to invalidate our conclusions. While an error of 0.1 milligram in the weight of the water involves an error of about 1.5 cubic centimeters of water vapor at 1,200°, this becomes relatively unimportant, since the total water vapor is seldom less than several hundred cubic centimeters. Consequently an error of a milligram would still allow fairly sound inferences. For sulphur and chlorine an error of 0.1 milligram involves a volume error of about 0.2 cubic centimeter at 1,200°, and for fluorine about 0.4 cubic centimeter. These errors are all within permissible limits, though improvements in this part of the system are much to be desired.

In the gasometric methods, the most serious cause of error is leakage, and this can be avoided by constant checking up of the apparatus before and during the analysis. Adsorption effects may be serious, but with the reagents here recommended they are minimal, and if the precaution is observed of always keeping the glass surfaces clean and dry, such effects will not be disturbing, although at times they may make the work tedious.

In practice we have found that the setting of the volume-bulb contact and reading of the barometer to 0.1 millimeter is not difficult. Though here we allow an error of ±0.1 millimeter, about 80 per cent of our settings show a smaller error. A total error of 0.2 millimeter at volume *D* (Fig 17) corresponds to about 0.003 cubic centimeter, and by shifting from the larger to the next smaller volume with corresponding magnification of the pressure as the analysis proceeds, a quite satisfactory degree of accuracy can be maintained. This, of course, implies that the volume bulb was care-

fully calibrated and the zero points of the barometer scale are kept verified, as should be done.

If the apparatus is always exhausted to the same degree of vacuum, namely, 0.001 millimeter, there is no difficulty in passing an inert gas through any of the reagents and, upon returning it to the volume bulb, observing the same value within the limits of reading-error. The apparatus is therefore sufficiently accurate for the

TABLE I

VOLUME PERCENTAGES AT 1,200° AND 760 MM.

P	CO_2	CO	H_2	N_2	A	SO_2	S_2	Cl_2	F_2	H_2O	cc./g.
P1919*a*.....	11.757	0.148	0.376	0.280	tr	0.000	1.662	1.334	3.609	80.834	6.9 cc.
P1919*b*.....	11.172	0.045	0.464	1.305	tr	0.008	1.670	1.030	6.203	78.100	7.3

purposes for which it was developed, and considerably more accurate than the methods of collecting these gases from their sources have yet become.

As we have already indicated, not only do vacuum-tube collections suffer from contamination by the surrounding atmosphere, but also some loss is unavoidable in sealing off the tips. On the other

TABLE II

EXPRESSED IN ATOMIC PERCENTAGES

P	C	H	O	N	A	S	Cl	F
P1919*a*.....	4.071	55.501	35.713	0.191	tr	1.136	0.912	2.467
P1919*b*.....	3.886	54.407	34.803	0.904	tr	1.159	0.546	4.296

hand, in the extraction of these gases from the rocks *in vacuo* we have to consider not only the uncontrollable rate of evolution of the less volatile constituents, but also the unpredictable rearrangements among the gases caused by the rate of pumping and catalytic or surface effects. In this connection Tables I and II, showing parallel runs for the same Kilauea lava, are instructive. We must note here that the large amount of water in both gases smooths out these relations, but the essential point is that the results are as reproducible as the material with which we have to work.

METHOD OF STATEMENT OF RESULTS

Some comment seems desirable as to the reasons for expressing our results as we have been doing. First, let us dispose of the notion that we are overestimating the accuracy of our analytical procedure because we compute the figures to the third decimal place. This extension of decimals is due to the fact that about 80 per cent of water has to be added in the final computation. For example, let us suppose that in the analysis we end with a pressure of 142 millimeters for argon at the *A* volume. Naturally with such a small quantity of gas it can be more accurately determined at one of the smaller volumes of the volume bulb. This pressure of 142 millimeters corresponds to about 0.5 millimeters pressure at the *D* volume, the one at which the other constituents have been determined. This is obviously a determinable amount of argon, and it amounts to about 0.015 cubic centimeter of gas at 0°, 760 millimeters, or about 0.08 cubic centimeter at 1,200°. This value, however, is added in with the volumes obtained for the other gases, among which there is usually several hundred cubic centimeters of water vapor, so that if the argon which is certainly present is to be shown at all in the result, the decimals must be extended.

In computing the results, certain assumptions are necessary. One assumes the strict applicability of the usual gas-law equation, and that a gram molecule of any gas occupies 22,412 cubic centimeters at 0°, 760 millimeters. The essential equations for computing results are:

$$A=\frac{1 \text{ gram molecule}}{22412}=\text{weight in grams of 1 cc. at 0°, 760 mm.}$$

$$A\times\frac{273}{1473}=\text{weight in grams of 1 cc. at 1,200°, 760 mm.}$$

From these we obtain the necessary figures for transposing the results for any gas into grams or cubic centimeters as required. In computing the analysis, the fixed gases are obtained in cubic centimeters at 0°, 760 millimeters, and these figures transposed to cubic centimeters at 1,200°, 760 millimeters by the usual formula

$$\text{cc. at 0°, 760 mm.}\times\frac{1473}{273}=\text{cc. at 1,200°, 760 mm.}$$

The weight in grams of these volatiles determined gravimetrically is to be divided by the weight of 1 cubic centimeter at 1,200°, 760 millimeters, to give their volumes at 1,200°, from the total of which the volume percentage is computed.

We have also been taken to task because our figures are not readily comparable with those of previous investigators. Some standard must be selected at which these components are gases, and since the temperatures at which lavas reach the air are of the order of 1,200°, it seems reasonable to select a temperature of 1,200° and 760 millimeters as a standard for comparison of such gases. At this temperature both water and sulphur may be treated as gases. Since, however, previous investigators have almost without exception ignored water, halogens, and usually sulphur, and since the relations between hydrogen, water, and the oxides of carbon are so intimate, there seems no very good reason for attempting comparisons with other published results. A glance at the tables collected by Dr. E. T. Allen[1] will satisfy one that there is little common ground for such comparison.

It is perhaps less excusable to compute fluorine and chlorine as elementary, but there seems no very good reason to assign the appropriate hydrogen to them in view of their activity at the temperatures in question. Boron has been omitted from the list of volatiles pending the discovery of some satisfactory method of determination in the presence of all these other elements.

The variable and perhaps surprising amount of fluorine in the above gases is really not as improbable as it at first seems. It is one element which is never determined in rock analysis, though its presence is admitted, and the amount is usually small. As a volatile, however, it is not fairly neglected, since in volume it not infrequently equals or exceeds carbon dioxide. When referred to the weight of rock taken, it falls into line again. Thus, in the above analyses the fluorine, expressed as weight percentages of the rock taken, appears as 0.0012 and 0.0021 respectively for *a* and *b*. In our determinations thus far it varies from about half to twice the amount of chlorine by

[1] Chemical aspects of volcanism," *Jour. Franklin Inst.*, Vol. CXCIII (1922), pp. 70–80.

weight, a fact that should be of some interest to geologists interested in the relation between weathering and salt deposits.

For purposes of comparison, we need several arrangements of these analyses. Atomic percentages allow the best comparison of the fundamental composition. The volume percentages give some insight into the degree of oxidation and therefore must be included.

Since the volatiles, except in some measure chlorine and sulphur, are not included in ordinary rock analyses, it is often desirable to add also the weight percentages of the rock. This naturally involves a great many decimal places, although the values are real enough. In the Table III we have endeavored to give as complete information as available concerning a glassy andesite from Lassen Peak. This was the material extruded in 1915. The mass as a whole is variable in composition, but the determinations given in the table apply to one fairly uniform block. The rock analysis was made by M. Aurousseau, to whom we express our thanks.

It will be noted that the total volatiles amount to only 0.15 per cent of the weight of the rock, although at 1,200° each kilo of lava is still able to furnish about 10 liters of gas. There is an obvious discrepancy between the figures for water as determined in the analysis of the rock using powdered material and the water obtained *in vacuo* using rock chips. The latter figure probably represents the actual water content of the rock, and for this material it appears that in the grinding operations the apparent water content has been doubled. The same is true of the Hawaiian and Martinique lavas, as shown in Table IV.

The first column gives the weight percentage of water for these lavas as extracted *in vacuo*, the second column the water content of the same material after grinding for analysis. There is no doubt about the accuracy of either set of figures. It appears, therefore, that the unavoidable grinding operations in preparing a rock for analysis approximately double the water content, and this adsorbed water is not given off at 110°. This is not news, since Day and Allen, working with pure quartz, found that the adsorbed water was not completely removed at 500°. It may be added that in these vacuum determinations and working with dry chips of rock, about 3 per cent

of the water is evolved below 200°, about 30 per cent between 200° and 700°, while about 67 per cent is released between 700° and 1,200°.

TABLE III

ANDESITE (NEAR DACITE) LASSEN PEAK, CALIFORNIA. LAST PRODUCT OF EXTRUSION, 1915

ROCK ANALYSIS			WEIGHT PERCENTAGE OF ROCK	VOLUME PERCENTAGE AT 1200°		ATOMIC PERCENTAGES
Constituents	Percentage					
SiO_2	63.21	CO_2	0.00906	2.070	Carbon	0.914
Al_2O_3	17.15	CO	0.00137	0.623	Hydrogen	63.508
Fe_2O_3	1.30	H_2	0.00003	0.412	Oxygen	33.352
FeO	3.00	N_2	0.00127	0.577	Nitrogen	0.389
MgO	2.96	A	0.00001	0.003	Argon	0.001
CaO	5.23	SO_2	0.00047	0.009	Sulphur	0.602
Na_2O	4.12	S_2	0.00376	0.882	Chlorine	0.201
K_2O	2.10	Cl_2	0.00166	0.297	Fluorine	1.033
H_2O+	0.31	F_2	0.00457	1.524		
H_2O-	0.04	H_2O	0.13327	93.658	Total	100.000
CO_2	none					
TiO_2	0.48	Total	0.15347	9.5 cc/g		
ZrO_2	0.02					
P_2O_5	0.16					
Cl	0.02	NORM				
F	p.n.d.					
S	0.03			Percentage		
Cr_2O_3	trace					
MnO	0.07	Quartz		15.18		
BaO	0.07	Orthoclase		12.23		
SrO	.....	Albite		34.58		
Li_2O	.....	Anorthite		22.24		
		Diopside		2.26		
Total	100.27	Hypersthene		10.00		
Less	0.01	Ilmenite		1.06		
		Magnetite		1.86		
Total	100.26	Apatite		0.34		
		Water		0.35		
		Total		100.00		

Symbols, (I) II.4″.3.4.
Tonalose

Mode.—Plagioclase about 15 per cent, biotite 3 per cent, pyroxene 2 per cent, quartz less than 1 per cent, some magnetite, and the rest glass. Plagioclase irregularly shattered and zoned, varying between Ab_3An and Ab_1An_1. None of the phenocryst feldspar as calcic as some of the ground mass. Pyroxene near diopside; lowest, $\alpha = 1.675$, highest, $\gamma = 1.715$; in shattered aggregates. Biotite, always surrounded by reaction rims and showing loss of volatiles, reaches $\gamma = 1.70$ with $2E = 10°$ to 40°. Quartz occurs as a few corroded grains. The ground mass is a highly siliceous glass with an index varying between 1.485 and 1.500 at points but little separated. The glass is brownish in thin section with needles of pyroxene and plagioclase, the latter reaching the composition Ab_3An_1. The glass is full of microscopic crystals.

In any series of runs on the same material, it will be found that while the carbon, hydrogen, and oxygen will be fairly constant, the halogens and sulphur will vary, and this variation will be in large measure determined by the temperature of extraction and the time during which this temperature is maintained. Thus we observe that for the heavier constituents our methods do not permit a quantitative determination of the total amount in the rock unless special pains are taken to arrive at such a result. On the other hand, the method allows a fairly accurate determination of the volatiles which are given off at the temperature in question, and therefore

TABLE IV

CHANGE OF H_2O CONTENT DUE TO GRINDING ROCK FOR ANALYSIS

Specimen No.	From Coarse Fragments *in Vacuo*	From Powder Ground in Air
	Per Cent	Per Cent
DA	0.15	0.31
P1911	0.07	0.17
MP/1	0.06	0.68
MP/5	0.06	0.25
MP/6	0.04	0.11
MP/7	0.38	0.42

of the composition of the gases which such a rock would release if reheated, or if, while hot, it were moved into a region of lower pressure.

SUMMARY

Methods are described for collecting and analyzing the volatile matter from volcanoes and from rocks heated *in vacuo*. The methods are described in detail and their limitations indicated.

The form in which such results are to be expressed is indicated, and the insufficiency of the data obtained by earlier investigators discussed. The elaborateness of the data required in order that such results may be of any service has been explained and a typical record given. It is the writer's opinion that the volatiles obtained from a systematically collected series of lavas will throw quite as

much light on the nature of the crater reactions as we may hope to obtain from gases collected at the crater during eruption.

It should be noted that we do not regard the present apparatus as final. It has been developed over a period of years, and this description is published partly in response to inquiries about the methods used. These methods are by no means as simple or precise as we could wish, but they seem sufficient.

The writer is under great obligations to all of his colleagues at the Geophysical Laboratory, and in particular to Dr. H. E. Merwin, for advice and assistance.